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THE RESULTS OF THE 22nd CONGRESS OF THE COMMUNIST PARTY OF THE SOVIET UNION

Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 12, pp. I-II, December, 1961

One of the most outstanding events in the history of the world Communist movement and in the history of our country was the 22nd Congress of the Communist Party of the Soviet Union. The Congress adopted a new program for the Party, warmly approved by the representatives of 80 foreign Marxist-Leninist Parties present at the Conference, and demonstrated the unity of the Socialist camp, the solidarity of the Communist and Workers' Parties, the common purpose of workers throughout the world.

In the report of the Central Committee of the Communist Party of the Soviet Union, Comarade N. S. Krushchev dealt with the present-day world situation and the international position of the Soviet Union and reported to the Congress on the activity of the Party after the 20th Congress: on the struggle to perform the main tasks in the building of Communism and on the creation of a material and technical base for Communism, on the further securing of the economic power of the USSR. "In the development of the economy we have made considerable progress and we are firmly proceeding along the Leninist road, scaling one height after another. We are nearing our great objective and we can already see the brilliant peak on which in the near future the Soviet nation will erect the banner of Communism."*

The building of Communism in our country involves starting new plants, electric power stations, scientific institutes providing an abundance of agricultural products and other material wealth. In the epoch of the building of Communism, in the creation of a material and technical base, far-reaching changes are made in the system of organizing production — on the basis of the development of technical sciences, complex mechanization and extensive automation are being introduced, and power supplies are being increased. The ever increasing practical use of the achievements of chemistry has brought fundamental changes into the character of material produced by the industry, including consumer goods and the chemicalization of argiculture sharply increases its productivity. Nowadays science and production are linked together since modern production could not continue without science. Production, in the words of Marx, to an increasing extent involves the technological application of science. Communism, having expanded the practical application of science, makes it a deciding factor in the growth of production forces of society and science is therefore embodied in the technology of production, it is converted to a direct production force for society. Whereas at present most workers only need laboring and production experience, in the building of Communism an ever increasing number of workers should also have scientific knowledge. When mental and physical effort are combined in the production activity of the people and the barrier between the intelligentsia, the workers and the peasants disappears forever then the man of the Communist society will appear — well balanced, widely educated, with high ideals, free from the survivals of bourgeois views of our science as follows: "Science is called to answer the problems of the present day, to serve as a fighting weapon in the solution of the most pressing economic problems, in the development of the production forces of society. In the broad view science should open up possibilities for controlling thermonuclear reactions for the peaceful use of unlimited sources of nuclear energy, to act on the climate and weather conditions, to fight illness and give mankind long life, to direct the life processes of organisms, to create a limitless number of synthetic materials with required properties, to conquer space, to set up reliable means of communication in the universe. This will form a whole epoch in the world history of science and technology, will give man inexhaustible resources of energy, will make him truly a master of nature"... "The honor and patriotic duty of Soviet scientists is to consolidate for Soviet science the leading positions in the most important fields of knowledge which have already been won and to give it a leading role in world science in all important fields."**

* Report of the Central Committee of the Communist Party of the Soviet Union to the 22nd Congress of the Party [in Russian] (State Political Press, 1961) p. 49.

** On the Program of the Communist Party of the Soviet Union [in Russian] (State Political Press, 1961) p. 98.

We would not have made those great achievements in the field of physics, chemistry, biology and the mastery of space if from the very first years of Soviet power our science had not been linked with life and the production labor of the people in the closest way possible. The role of science in the building of a new society was indicated by V. I. Lenin when he directed the activity of the Academy of Sciences to solve the most important scientific and technical problems. At the present time when the role of science has grown, the scientists present at the General Conference of the Academy of Sciences of the USSR, discussing the results of the 22nd Congress of the Party, were given illustrations of the effect of new ideas and theoretical achievements on the development of the most recent technology and technological processes in chemistry based on new principles.

The further development of theoretical investigations will permit Soviet scientists to still further accelerate technical progress in all branches of industry and in agriculture. However, there should be drastic reductions in the time from the completion of the investigation to the adoption of its results in industry. Here much depends on the scientists themselves and the degree of prefection of their scientific work as well as on the workers in industry and the vigorous collaboration from the State Committees of the Councils of Ministers on the coordination of scientific research work. The state plans of scientific research, experimental work and work introduced into production should also be performed properly so that the production plans of our industry can be fulfilled.

In the solution of problems placed before science by the 22nd Congress of the Party a tremendous role should be played by young scientific groups, of which there are too few in the administrative work in the Academy of Sciences. The work of the greatest scientists must be correctly combined with the timely emergence of a talented youth and the formation from it of a number of vigorous organizers of science, who know and love their work.

The Reports of the 22nd Congress of the Party will be studied attentively by all Soviet Scientists, who are making every effort to give their ability and knowledge to the service of the nation and to fulfill the resolutions of the historic tasks presented in the program of our party and unanimously approved by the 22nd Congress.

A PHYSICOCHEMICAL STUDY OF THE REACTION BETWEEN PRASEODYMIUM HYDROXIDE AND HYDROGEN PEROXIDE

S. Z. Makarov, L. V. Ladeinova-Soboleva, and

A. M. Chernyshova

N. S. Kurnakov Institute of General and Inorganic Chemistry,
Academy of Sciences, USSR
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In the rare earths compounds are usually formed in the trivalent state. Cerium, praseodymium and terbium can form compounds in the quadrivalent state and samarium, europium and ytterbium can form compounds in the divalent state. In the quadrivalent state praseodymium is only found in the higher oxides Pr_6O_{11} and PrO_2 [1]. The higher oxides of praseodymium are strong oxidizing agents but they do not exhibit reactions which are characteristic for peroxides [2].

As yet there is insufficient clarity as to the nature of oxygen present in the higher oxides of praseodymium, cerium, terbium and which some workers refer to as "active oxygen." From the paper of Malaguti [3], dealing with the determination of "active oxygen" in the higher oxides of praseodymium and cerium it follows that the "active oxygen" refers to the amount of oxygen combined with Ce^{4+}, Pr^{4+}, Tb^{4+} and exceeding the oxygen which should be combined with Ce^{3+}, Pr^{3+}, Tb^{3+}. This excess oxygen is reduced by an equivalent amount of reducing agent (H_2O_2, $FeSO_4$, etc.) and is not therefore peroxide oxygen.

In some papers [2, 3] it has been shown that the higher oxides of praseodymium are not peroxide compounds. Recently a paper by Foex and Loriens appeared [4] in which the PrO_2 and Pr_6O_{11} are persistently referred to as peroxides. For praseodymium peroxide Brauner [5, 6] proposes the formula: Pr_2O_5.

Melikov and Klimenko [2] prepared praseodymium peroxide by dissolving praseodymium nitrate or sulfate in hydrogen peroxide and then carefully adding a weak solution of ammonia (or KOH). The hydrate of praseodymium peroxide was then obtained as a gelatinous pale green precipitate. The authors noticed the partial decomposition of the product accompanied by the evolution of active oxygen and they represent the formation of praseodymium peroxide in the following way: at first (in the terminology of the authors) "triple peroxide hydrate of praseodymium" is formed – $Pr(OOH)_3$, which is decomposed with the evolution of free oxygen to the "monoperoxide hydrate" $Pr(OOH)(OH)_2$. Chemical analysis of praseodymium peroxide, according to the authors, indicates that it is Pr_2O_5 but they do not give formulas for expressing the hydrate of praseodymium peroxide. When the hydrate of praseodymium hydroxide is dried over H_2SO_4 there is a loss in water and active oxygen. The authors consider that the trihydrate of praseodymium peroxide is formed in which one OH group is replaced by OOH. According to Melikov and Klimenko praseodymium peroxide is a derivative of hydrogen peroxide; when weak H_2O acts on it H_2O_2 is liberated and when concentrated H_2SO_4 acts on it ozone is liberated.

EXPERIMENTAL

By analogy with previous papers on the investigation of peroxide compounds of Ce, La, Nd we studied peroxide compounds of praseodymium as products of the reaction of $Pr(OH)_3$ with hydrogen peroxide at 0 and −20°. As previously [7, 8], we used the solubility method, which makes it possible to determine more completely the compositions of the liquid and solid phases according to the method of residues by comparison with the method of Billy and San-Galli [9], who only analyzed the liquid phase. The data of the investigation were plotted on a triangular diagram of $Pr_2O_3-H_2O-\frac{1}{2}O_2$. In view of the fact that roasting praseodymium oxalate in air (the analytical method for determining Pr in the residue and in the liquid phase) gives black Pr_6O_{11}, to plot the data on the $Pr_2O_3-H_2O-\frac{1}{2}O_2$ diagram there was conversion from Pr_6O_{11} to Pr_2O_3.

Praseodymium hydroxide $Pr(OH)_3$ was obtained from a solution of $Pr(NO_3)_3$ (1.5 g of salt in 70 ml H_2O) by precipitation with a hot solution of ammonia (150 ml, sp. gr. 0.998). The light green gelatinous precipitate was washed with hot water. The washed precipitate was dried in vacuum at room temperature and ground to a fine powder. The differential heating curve for the prepared praseodymium hydroxide (Fig. 1) has a combined endothermic effect in the temperature range 312-360°. Pure hydrogen peroxide without a stabilizer was prepared by distilling perhydrol in a vacuum apparatus. The praseodymium in the residue and in the liquid phase was determined gravimetrically: by preliminary precipitation with oxalic acid and subsequent roasting to praseodymium oxide of composition Pr_6O_{11} with conversion to Pr_2O_3. The active oxygen in the residue and in the liquid phase was determined by titration with a 0.1 N solution of $KMnO_4$ in a sulfuric acid medium.

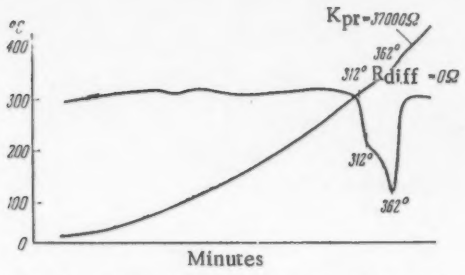


Fig. 1. Differential heating curves for praseodymium hydroxide.

Reaction of Praseodymium Hydroxide with Hydrogen Peroxide at 0 and −20°

The arrival of equilibrium in the reaction between $Pr(OH)_3$ and H_2O_2 was located: a) by the constancy of the composition of the liquid phase and b) by constancy of composition of the obtained solid phase. The least time required to establish equilibrium between the chemical compositions of the liquid and solid phases was found to be 2-3 hr and is shown in Table 1.

The reaction between praseodymium hydroxide and hydrogen peroxide at 0° was studied between 0.00 and 93.41% H_2O_2 in the liquid phase and it was considered, from the point of view of formation of solid phases, in the ternary system $Pr(OH)_3-H_2O_2-H_2O$. The data of the investigation are given in Table 2 and in Figs. 2, 3. From 0.0 to <3.95% H_2O_2 $Pr(OH)_3$ exists. With hydrogen peroxide concentrations between 3.95 and 91.78% one solid phase of the peroxide type is formed with general composition $Pr_2O_4 \cdot 2H_2O$. Above 92% H_2O_2 in the liquid phase the residues decompose. On the solubility curve (Fig. 3) there were branches corresponding to $Pr_2O_4 \cdot 2H_2O$ and decomposed residues. The branch corresponding to $Pr(OH)_3$ is not accurate.

TABLE 1. Establishing the Time of Arrival of Equilibrium in the Reaction between $Pr(OH)_3$ and H_2O_2 at −20°

Time, hr	Composition of liquid phase, weight %			Comp. of residue, weight %		Solid phase
	act. O_2	H_2O_2	Pr_2O_3	act. O_2	Pr_2O_3	
0	19,68	41,84	—	—	—	—
1	18,79	39,95	0,143	10,63	49,19	$Pr_2O_4 \cdot 2H_2O$
3	18,63	39,65	0,141	12,30	40,59	The same
4	17,75	37,74	0,116	12,23	39,77	» »

At −20° the investigation was carried out in a range of hydrogen peroxide concentrations of 25, 75-95, 35% in the liquid phase (Table 3, Figs. 4, 5). With up to 26% H_2O_2 in the liquid phase ice crystallizes. Within the limits of H_2O_2 in the liquid phase of 25, 75-49,30% the solid phase $Pr_2O_4 \cdot H_2O$ appears, which can be considered as the product of dehydration of $Pr_2O_4 \cdot 2H_2O$. At higher concentrations of H_2O_2 in the liquid phase there is decomposition with a reduction in the solubility of the praseodymium. The residues corresponding to $Pr_2O_4 \cdot 2H_2O$ and $Pr_2O_4 \cdot H_2O$ were washed with alcohol and ether and dried over phosphoric anhydride in a desiccator (Table 4).

The data show that during dehydration products are obtained which are close in composition to $Pr_2O_4 \cdot$ (4 and 6) H_2O and $Pr_2O_5 \cdot 5H_2O$. However, the peroxide compounds of praseodymium, like lanthanum and neodymium are not completely dehydrated under these conditions.

The differential heating curves of the "residues" of $Pr_2O_4 \cdot 2H_2O$ and $Pr_2O_4 \cdot H_2O$ (Table 5) taken on the Kurnakov recording pyrometer with a Pt-Pt Rh-termocouple with a rate of heating of 4°/min, together with the volume of liberated oxygen, showed the complex character of the thermograms.

TABLE 2. Data of Reaction between $Pr(OH)_3$ and H_2O_2 Solutions at 0°

No. of expt.	Composition of liquid phase, weight %			Composition of residue, weight %		Solid phase
	act. O_2	H_2O_2	Pr_2O_3	act. O_2	Pr_2O_3	
29	0,00	0,00	0,050	—	—	$Pr(OH)_3$
13	1,86	3,95	0,017	2,98	44,60	$Pr_2O_4 \cdot 2H_2O$
12	4,06	8,63	0,031	4,15	47,77	The same
11	6,74	14,32	0,027	5,61	48,50	» »
4	9,14	19,43	—	6,88	49,47	» »
5	12,54	26,66	0,066	7,90	49,84	» »
19	16,13	34,29	—	9,77	45,76	» »
28	19,80	42,09	0,078	11,80	42,68	» »
22	22,46	47,75	0,070	12,47	44,16	» »
21	24,91	52,95	0,083	13,47	48,31	» »
24	27,90	59,31	0,091	16,93	40,58	» »
14	29,97	63,71	0,046	16,93	44,00	» »
26	33,81	71,88	0,078	17,93	46,42	» »
23	35,64	75,47	0,045	—	—	» »
15	38,21	81,02	0,070	20,49	44,89	» »
27	41,07	87,31	0,031	16,42	58,22	» »
18	43,17	91,78	0,013	22,65	39,95	Decomposed
25	43,94	93,45	0,019	23,89	42,70	»

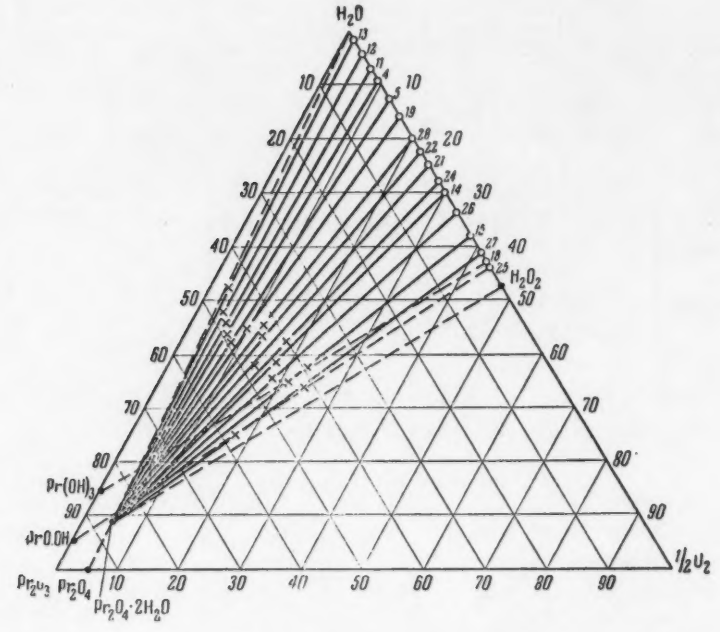


Fig. 2. 0° Isotherm of the system $Pr(OH)_3 - H_2O_2 - H_2O$.

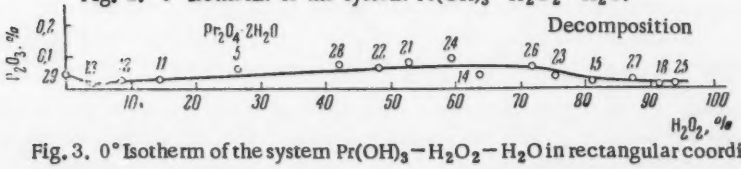


Fig. 3. 0° Isotherm of the system $Pr(OH)_3 - H_2O_2 - H_2O$ in rectangular coordinates.

TABLE 3. Data of Reaction between $Pr(OH)_3$ and H_2O_2 Solutions at −20°

No. of expt.	Composition of liquid, phase wt., %			Composition of residue, wt., %		Solid phase
	act. O_2	H_2O_2	Pr_2O_3	act. O_2	Pr_2O_3	
2	12,10	25,75	0,102	8,57	44,64	$Pr_2O_4 \cdot H_2O$
15	14,41	30,63	0,116	9,31	47,94	$Pr_2O_4 \cdot H_2O$
14	16,95	36,03	0,126	10,73	45,77	The same
17	19,45	41,35	0,140	12,11	39,53	» »
4	20,77	44,16	0,067	12,46	46,18	» »
5	23,19	49,30	0,029	12,00	44,80	Decomposed
16	24,09	51,22	0,078	—	—	»
3	27,88	59,27	—	12,86	53,08	»
20	33,62	71,47	0,019	15,78	46,66	»
7	34,13	72,53	—	10,11	57,78	»
8	38,24	81,30	—	8,29	61,87	»
18	38,78	82,45	0,0183	15,20	51,42	»
19	44,85	95,35	0,054	18,30	57,80	»

TABLE 4. Data on the Dehydration of "Residues" of $Pr_2O_4 \cdot 2H_2O$ and $Pr_2O_4 \cdot H_2O$

Residue corresponding to solid phase	Composition of residue, weight %			Composition of residue, molar			Composition of liquid phase, weight %		Formula
	act. O_2	Pr_2O_3	H_2O	act. O_2	Pr_2O_3	H_2O	act. O_2	H_2O_2	
$Pr_2O_4 \cdot 2H_2O$ init.	8.65	54.34	37.01	3.28	1.00	12.46	16.55	35.18	—
After washing with alcohol, ether	8.97	72.86	23.17	1.12	1.00	5.82	—	—	$Pr_2O_4 \cdot 6H_2O$
$Pr_2O_4 \cdot 2H_2O$ init.	20.55	47.63	30.82	8.92	1.00	11.89	39.12	83.17	—
After washing with alcohol, ether	6.64	72.98	20.38	1.88	1.00	5.12	—	—	$Pr_2O_{4.9} \cdot 5H_2O$
$Pr_2O_4 \cdot 2H_2O$ init.	9.36	48.02	42.62	3.93	1.00	15.88	14.77	30.76	—
After washing with alcohol, ether, drying over P_2O_5 at 4°	3.54	78.85	17.61	0.97	1.00	4.09	—	—	$Pr_2O_4 \cdot 4H_2O$

TABLE 5. Chemical Compositions of the Liquid Phases and Residues Corresponding to the Solid Phases $Pr_2O_4 \cdot 2H_2O$ and $Pr_2O_4 \cdot H_2O$

Solid phase	Composition of residue weight %			Composition of liquid phase, weight %	
	act. O_2	Pr_2O_3	H_2O	act. O_2	H_2O_2
$Pr_2O_4 \cdot 2H_2O$	8,37	49,37	42,26	13,24	28,15
$Pr_2O_4 \cdot H_2O$	10,38	54,22	35,40	16,44	34,95

On the differential heating curves of the "residue" of $Pr_2O_4 \cdot 2H_2O$ (Fig. 6) there can be seen: the first exothermic effect at 25-47.5°, the second exothermic effect at 95-97.5° and an endothermic effect finishing at 100°. The change in the chemical composition of the $Pr_2O_4 \cdot 2H_2O$ residue is shown in Table 6.

These data indicate that during the first exothermic effect it is most probable that active oxygen is evolved from the adsorbed hydrogen peroxide. Later the praseodymium peroxide decomposes with the simultaneous liberation of active oxygen and the removal of water (> 100°). The exothermic and endothermic effects are super-

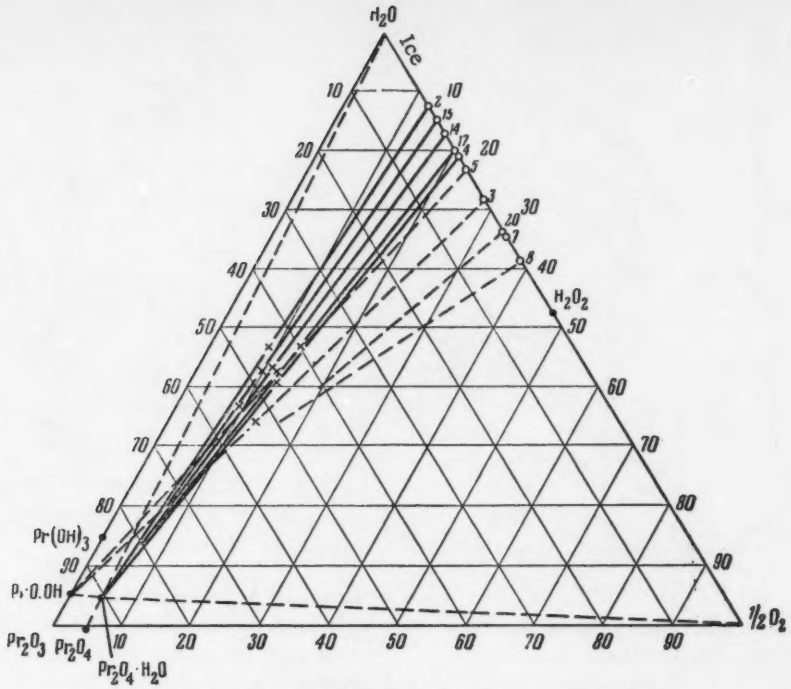


Fig. 4. −20° Isotherm of the system $Pr(OH)_3-H_2O_2-H_2O$.

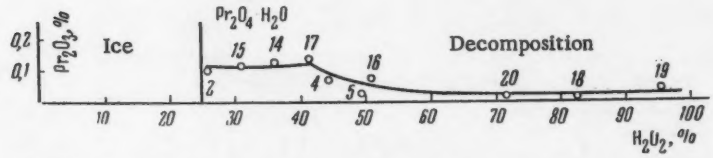


Fig. 5. −20° Isotherm of the system $Pr(OH)_3-H_2O_2-H_2O$ in rectangular coordinates.

TABLE 6. Data for Change in Chemical Composition of the $Pr_2O_4 \cdot 2H_2O$ "Residue" During Heating

Temperature, °C	Composition of product, weight %			Composition of product, molar			Formula
	act. O_2	Pr_2O_3	H_2O	act. O_2	Pr_2O_3	H_2O	
0	8,77	48,11	43,12	3,75	1,00	16,40	—
62	3,43	53,96	42,61	1,30	1,00	14,43	$Pr_2O_4 \cdot 14H_2O$
100	3,19	62,58	34,23	1,05	1,00	10,00	$Pr_2O_4 \cdot 10H_2O$
200	0,93	82,35	16,72	0,00	1,00	3,72	$Pr_2O_3 \cdot 4H_2O$

imposed on one another. The praseodymium hydroxide remaining due to decomposition of the praseodymium peroxide does not give up its water, even at 200°. The character of the thermal decomposition of the $Pr_2O_4 \cdot H_2O$ "residue" is similar to the $Pr_2O_4 \cdot 2H_2O$ "residue" (Fig. 7). The temperature of the first exothermic effect 70-82° and that of the endothermic effect 95-100°.

It should be mentioned that the behavior of the obtained peroxide compounds of praseodymium during treatment with alcohol, ether and during heating is perfectly analogous to the behavior of the peroxide compounds of

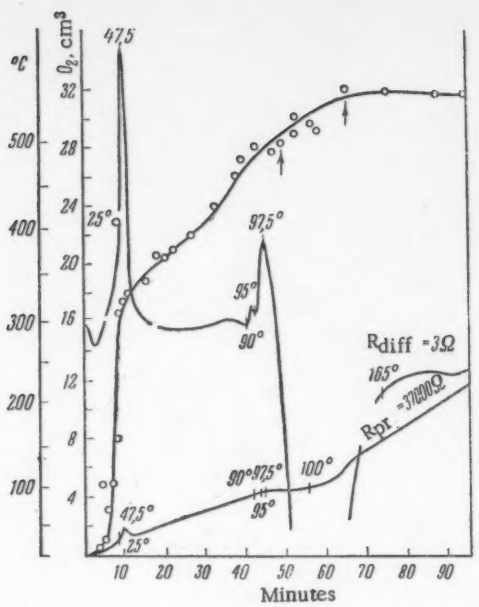


Fig. 6. Differential heating curves of residue corresponding to $Pr_2O_4 \cdot 2H_2O$.

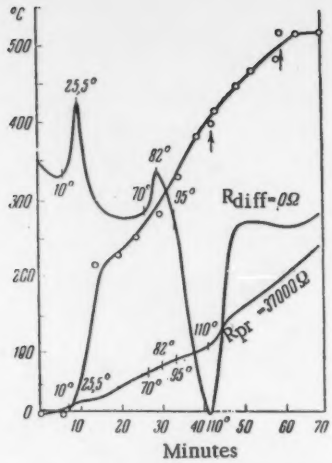
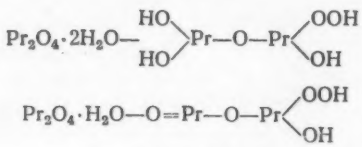


Fig. 7. Differential heating curves of residue corresponding to $Pr_2O_4 \cdot H_2O$.

lanthanum and may be due to their hydrogen peroxide nature. It can therefore be assumed that the solid phases of the peroxide type revealed during the investigation correspond to the following formulas:



SUMMARY

1. During the reaction between $Pr(OH)_3$ and H_2O_2 over wide concentration limits at 0 and −20° the existence of two solid phases of the peroxide type with general composition $Pr_2O_4 \cdot 2H_2O$ and $Pr_2O_4 \cdot H_2O$.

2. When these compounds are treated with alcohol, ether and heated there is no direct dehydration.

3. The solid phases formed during the reaction between $Pr(OH)_3$ and H_2O_2 should be considered as compounds of the hydrogen peroxide type.

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ADSORPTION AND HEAT OF ADSORPTION OF DIETHYL ETHER, ACETONE AND ACETIC ACID VAPORS ON GRAPHITIZED CARBON BLACK

N. N. Avgul', A. V. Kiselev, and I. A. Lygina

Institute of Physical Chemistry, Academy of Sciences of the USSR
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On graphitized carbon blacks with a homogeneous surface the adsorption and heat of adsorption has been studied for substances with nonpolar molecules (inert gases, hydrogen, deuterium, oxygen, and several saturated hydrocarbons), with molecules which, on the whole, are nonpolar but have a high quadrupole moment and a quite inhomogeneous distribution of the electron density (nitrogen, ethylene, benzene, carbon dioxide), for substances either unable (sulfur dioxide and ethyl chloride) or able to form mutual hydrogen bonds (ammonia, methyl amine, water, and alcohols). The high homogeneity of the surface of thermal blacks enabled us to come to a quantitative expression of these adsorptive properties in terms of physicochemical constants depending only on the nature of the system adsorbate-basal graphite face (see the review [1]).

In the present study we have investigated the adsorption of hydrocarbon derivatives containing oxygen, namely, diethyl ether, acetone and acetic acid. These substances have different properties. The diethyl ether molecule has a small dipole moment and in its geometric structure it is similar to hydrocarbons. The acetone mole has a very great dipole moment (μ $2.75 \cdot 10^{-18}$) [2]. These substances do not form hydrogen bonds. On the contrary, acetic acid forms strong mutual hydrogen bonds not only in the liquid but also in the vapor [3].

Adsorption of acetic acid on silicagel was investigated in the study [4]. By measuring the diamagnetic susceptibility it was shown that acetic acid molecules when adsorbed on silicagel do not form hydrogen bonds with the hydroxyl groups of the surface but interact with each other under the formation of cyclic dimers built up by hydrogen bonds. So, acetic acid molecules have a stronger tendency to form mutual hydrogen bonds than do even alcohols and water, which preferentially form hydrogen bonds with the hydroxyl groups of the silicagel surface [5, 6].

EXPERIMENTAL

The study was done with the thermal carbon black T1 graphitized at 3000° which has been investigated in [7-11]; its specific surface area s = 29 m^2/g. We used the purified adsorbates: diethyl ether ($n^{20}D$ 1.3479), acetone ($n^{20}D$ 1.3590; d^{20}_4 0.792 cm^3/g) and acetic acid (with freezing point 16.0°).

Just as has been done in [7, 8, 11] the differential heats of adsorption were measured at 20° in a calorimeter with constant heat exchange (model 1953 [12]), while the amounts of acetone and acetic acid adsorbed were determined by means of vacuum microburets for liquids [12] and that of ether by the gas volumetric method.

The adsorption isotherms of diethyl ether, acetone and acetic acid are shown in Fig. 1. Several series of experiments were done with each adsorbate. The adsorption is reversible. The adsorption isotherm of ether was only measured up to the relative pressure $p/p_s = 0.56$ because of its high vapor pressure p_s = 432 mm Hg. The adsorption isotherm of ether starts with a weakly concave and those of acetone and, in particular, acetic acid with a sharply concave part. In the intermediary range of p/p_s the usual shape of a polymolecular adsorption isotherm is found, while the adsorption isotherm of acetic acid in the polymolecular region rises particularly steeply.

In Fig. 2 the differential heat of adsorption Q_a is plotted versus the adsorbed amounts α of diethyl ether, acetone and acetic acid. At the start of monomolecular adsorption the heats rise with increasing coverages up to a maximum value Q_{max}. This rise is the greatest in the case of acetone and there it amounts to 1.5 kcal/mole. When one comes to the region where acetone is mainly adsorbed in the second layer, the heat of adsorption is found to fall to values close to the heat of condensation L, but for adsorption of acetic acid in a second and a third layer the net heat of adsorption Q_a-L still is considerable and amounts to ~1-0.5 kcal/mole.

Adsorption Isotherms

To decribe the adsorption isotherms we used the approximate equations derived for adsorption on homogeneous surfaces. Since the adsorption isotherms start with a concave part, which points to a considerable mutual attraction between the adsorbed molecules, this part of the isotherm is not described by the BET equation [13]. However, this equation does describe the convex parts of the isotherms at higher p/p_s. The monolayer capacities α_m calculated by the BET method, the corresponding values of the area occupied by one molecule in a filled monolayer $\omega_m = 1/\alpha_m N_0$, and even the range where the BET equation is applicable are given in Table 1. Upon passing from acetone to ether and acetic acid the said range becomes wider and this is in agreement with the variation in the net heat of adsorption Q_a-L.

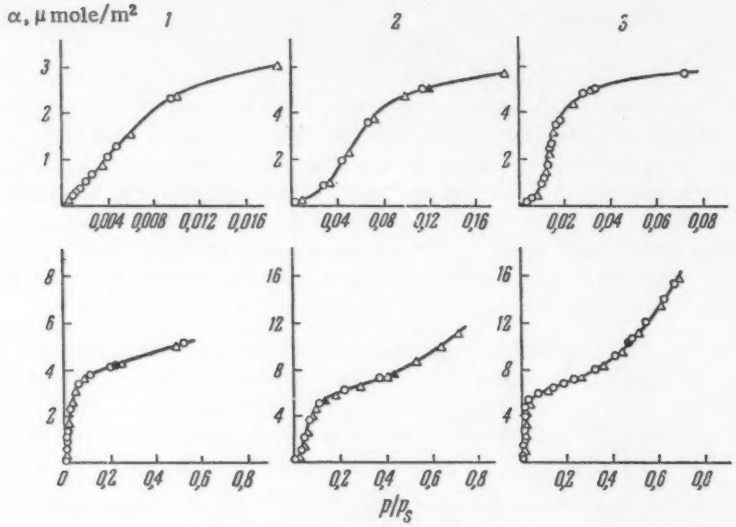

Fig. 1. Adsorption isotherms of diethyl ether (1), acetone (2) and acetic acid vapors (3) on the graphitized thermal black T1, 3000° at 20° plotted in two different scales. Here and further the filled points designate desorption.

From the van der Waals sizes of the molecules we have calculated the area which will be occupied by a flatly lying molecule in a complete monolayer and these values too are given in Table 1. Such a molecular packing may be realized, when the translational and some rotational and vibrational degrees of freedom are lost (at sufficiently low temperatures). For diethyl ether and acetone we did that calculation in [14]. In order to calculate ω_m for acetic acid we made a drawing of the molecule in the form of a dimer, while we used the interatomic distances, angles and van der Waals radii of groups and atoms, as are given in [7, 14, 15]. The densest packing of flatly lying dimers in a monolayer (Fig. 3) led to the value of 54 A^2 occupied per dimer or 27 A^2 when refered per molecule of monomer. Moreover, in Table 1 are given the values of ω_m calculated for a looser layer, in which vibrations along the surface and rotation are possible. These values were calculated from the area of the rectangle circumscribing the projection of the molecule (in the case of acetone and ether) or that of the dimer (in the case of acetic acid) onto the surface. The values found from the van der Waals sizes are close to those obtained from the BET equation. This indicates that the molecules of these three substances in a monolayer on the surface of the graphitized carbon black at 20° are packed flatly and quite densely.

For a more complete description of the adsorption isotherm, the initial concave part included, we applied the equations which have been derived for polymolecular adsorption on a homogeneous surface by approximately taking into account adsorbate-adsorbate interactions in the first layer and assuming localization [16] or free mobility [17].

When linearized the equation for localized adsorption has the following form:

$$\frac{z(1-p/p_s)}{p/p_s(1-z)} = K_1 + K_1K_n z, \tag{1}$$

and the equation for nonlocalized adsorption

$$V(z, p/p_s) = \frac{z}{1-z} + \ln\frac{z}{1-z} - \ln\frac{p/p_s}{1-p/p_s} = \ln K_1 + K_2 z, \tag{2}$$

where $z = \theta(1 - p/p_s)$, and $\theta = \frac{\alpha}{\alpha_m} = \frac{\omega_m}{\omega}$ — represents the degree of surface coverage. Besides the constant $\alpha_m = \frac{1}{\omega_m N_0}$, characterizing the packing and the equilibrium constant K_1 characterizing the adsorbate-adsorbent interaction, in these equations occurs a constant, K_n or K_2, characterizing the mutual interaction between adsorbate molecules in the first layer. The results obtained by applying the said equations to the adsorption isotherms are given in Figs. 4 and 5 and in Tables 2 and 3.

The calculations according to equations (1) and (2) were done by taking ω_m values which were varied for diethyl ether between 42 and 32, for acetone between 34 and 24 for acetic acid between 31 and 23 A^2. In Fig. 4 and the upper part of Fig. 5 the isotherms are plotted in the coordinates of equations (1) and (2), while in these figures we give the results found for that ω_m value for which the equations are obeyed over the widest range. Just these ω_m and the corresponding values of α are given in Tables 2 and 3. From these tables and Fig. 4 it is evident that for each adsorbate both equations are obeyed in about the same range, whereas for diethyl ether and acetic acid the equation of nonlocalized adsorption (2) is satisfied somewhat better. The deviations from equations (1) and (2) in the region of small coverages are caused by the residual inhomogeneity of the carbon black sample T1 (3000°) [9]. Furthermore, for all three adsorbates these equations only describe the monomolecular region of the adsorption isotherm, since upon passing to the second and following layers the mutual orientation of these complicated molecules changes and, therefore, the interaction between the adsorbed molecules will be changed too. However, in the case of acetic acid (Fig. 5) the cruve calculated by means of equation (2) is close to the experimental points even in the polymolecular region. In the paper [3] the formation of tetramers of acetic acid in the gas phase is pointed out. Therefore, it is possible that the acetic acid dimer molecules in the next layer form hydrogen bonds with the dimers in the underlying layer so that the adsorbate-adsorbate interaction changes little upon passing from the first to the next layers.

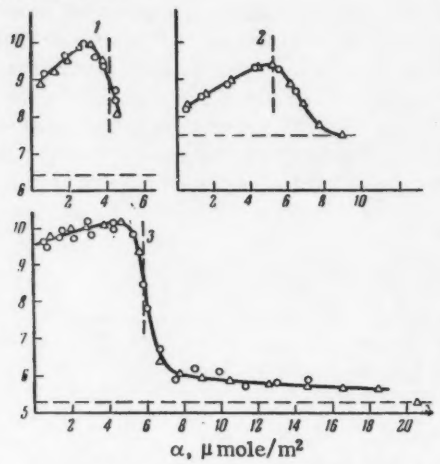

Fig. 2. The differential heat of adsorption Q_a plotted versus the adsorbed amounts α of diethyl ether (1), acetone (2) and acetic acid vapors (3) on the graphitized thermal black T1, 3000° at 20°. The horizontal dashed lines indicate the heat of condensation L, the vertical ones denote the capacities of a compact monolayer α_m.

Although both approximate equations, which are based on different adsorption mechanisms, are formally satisfied in about the same range of α, one should prefer that equation which is obeyed at the more probable values of ω_m. In the paper [8] we have shown that in the adsorption of methanol on carbon blacks graphitized to various extents one finds a transition from mainly localized to mainly nonlocalized adsorption of this weakly adsorbed substance, as one passes from the less to the more homogeneous surface. In the case of the strongly adsorbed substances investigated in this study, probably at the usual temperatures both mechanisms will occur. But from Tables 1 and 2 it is evident that in all cases the equation for localized adsorption is satisfied at values of ω_m close to those calculated from the van der Waals sizes of the molecules. However, the equation for nonlocalized adsorption is always better satisfied at smaller, often very improbable, values of ω_m, just as is

found for nitrogen and n-hexane adsorption [18]. It should also be kept in mind that equations (1) and (2) do not take into account a possible reorientation of the molecules at increasing coverage or a looser packing upon passing to the second layer. All these questions require further investigation; first of all, the isotherms must be measured over a broader temperature range and a more complete statistical thermodynamical discussion is needed [19].

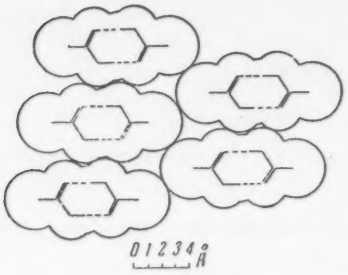

Fig. 3. Diagram showing dense packing of acetic acid dimers.

In the adsorption of diethyl ether, acetone and acetic acid the constant of the adsorbate-adsorbate interaction (K_n or K_2) is greater than one, which results in a concave start of the adsorption isotherm [16], while relatively the smallest adsorbate-adsorbate interaction is found for diethyl ether; since the molecules of the latter substance have a small dipole moment, their mutual attraction is for the main part only on electrokinetic (dispersion) forces. In the adsorption of acetone molecules with their very great dipole moment, the adsorbate-adsorbate attraction is higher owing to the much greater orientational interaction. In the adsorption of acetic acid the interaction between the monomers is particularly high, because dimers connected by hydrogen bonds are formed.

Heat of Adsorption and Energy of the Adsorptive Forces

Above it was noted that the rise in the differential heat of adsorption (Fig. 2) at increasing monolyaer coverages originates from the mutual interaction between the molecules in the adsorbed layer. By extrapolating the isotherm of the differential heats to zero amount adsorbed we are able to estimate the value of the heat of adsorption Q_0 for an adsorbate molecule when isolated on the adsorbent surface. We did this for molecules of various structures. The value of Q_0 for diethyl ether 8.9 kcal/mole is somewhat smaller than that of n-pentane 10.0 kcal/mole [20]. The structures of these molecules are nearly equal: passing from n-pentane to diethyl ether means that only the central CH_2 group of the former is replaced by an oxygen atom. A theoretical calculation of the energy for the dispersional and inductional interaction between graphite and diethyl ether or n-pentane gives $\overline{\Phi}_0'$ values equal to 9.4 and 10.2 kcal/mole, respectively [14, 21]. So, the difference between the heats of adsorption of diethyl ether and n-pentane on graphite is explained by the fact that the CH_2 group gives a greater contribution to the energy of the adsorptive forces than does an oxygen atom.

TABLE 1. Constants of the BET Equation and van der Waals Sizes of the Areas Occupied by a Flatly Lying Molecule ω_m

Adsorbate	Applicability limits of the BET equation		From the BET equation		From the van der Waals sizes of the molecules packed			
					most densely		loosely	
	in p/p_s	in α, $\mu M/m^2$	ω_m, A^2	α_m, $\mu M/m^2$	ω_m, A^2	α_m, $\mu M/m^2$	ω_m, A^2	α_m, $\mu M/m^2$
Diethyl ether	0.01-0.25	2.4-5.0	42	4.0	39	4.2	45	3.7
Acetone	0.1-0.3	4.8-6.5	34	4.9	31	5.4	41	4.0
Acetic acid	0.025-0.42	4.9-9.6	30	5.5	27	6.1	31	5.4

The rise of heat of adsorption from Q_0 to the maximum value Q_{max} originates from the energy of the mutual interaction between the adsorbate molecules. For diethyl ether Q_{max}-Q_0 amounts to 1.1 kcal/mole. Q_{max} occurs at an amount adsorbed where the diethyl ether molecules still form a quite loose monolayer: α = 3.1 μmole/m^2, and $\omega = 53A^2$. The fact that Q_{max} lies at $\omega > \omega_m$ indicates that in adsorption of molecules with a small dipole moment the completion of a monolayer is accompanied to a considerable extent by adsorption in the second layer too. Moreover, the reason for the loose packing of ether and n-alkane molecules [20] may even lie in their rotation around the long axis.

A theoretical calculation of the energy for the mutual dispersional interaction between diethyl ether molecules in a monolayer, Φ_{ii} at $\omega = 53$ A^2, gives 1.0 kcal/mole [14], whereas in this case the orientational interaction because of the small dipole moment is less than 0.1 kcal/mole.

TABLE 2. Range of Applicability and Constants of the Equation for Polymolecular Localized Adsorption (equation 1)

Adsorbate	Values taken		Range of applicability		K_1	K_n
	ω_m, A^2	α_m, $\mu M/m^2$	in p/p_s	in α, $\mu M/m^2$		
Diethyl ether	42	4.0	0.001-0.02	to 3	53	3
Acetone	28	5.9	0.03-0.15	1-5.5	1.2	24
Acetic acid	26	6.4	to 0.04	to 5	4	33

TABLE 3. Range of Applicability and Constants of the Equation for Polymolecular Nonlocalized Adsorption (equation 2)

Adsorbate	Values taken		Range of applicability		K_1	K_2
	ω_m A^2	α_m, $\mu M/m^2$	in p/p_s	in α, $\mu M/m^2$		
Diethyl ether	32	5.2	0.001-0.005	to 4	44	3.2
Acetone	24	6.9	0.03-0.15	1-5.5	3	5
Acetic acid	24	6.9	to 0.15	to 6.5	7.5	6.5

Let us compare the values of Q_0 for acetone and n-propanol [7]. Both C_3H_6O and C_3H_8O have flat molecules and consist of nearly the same atoms, which are grouped differently. One would expect nearly the same values for the heat of adsorption of isolated molecules, but for acetone $Q_0 = 8.0$ kcal/mole and for n-propanol $Q_0 = 12.8$ kcal/mole. This difference is explained by the fact that in adsorption of n-propanol even at small coverages there are formed associated groups of molecules connected by hydrogen bonds [7]. This is also pointed out by a theoretical calculation of the adsorption energy of isolated molecules on the surface of a basal graphite plane [7, 14]. For acetone $\bar{\Phi}_0'$ amounts to 8.1 kcal/mole, that is, the dispersional and inductional interactions of both molecules with a graphite surface are nearly equal. So, in the adsorption of n-propanol there exist other additional adsorbate-adsorbate interactions (hydrogen bonds). An acetone molecule has a great dipole moment, therefore, one should expect a dense packing of acetone molecules in a monolayer. In fact, Q_{max} is found at $\omega = 32$ A$^2 \approx \omega_m$ corresponding to a densely packed layer.

A calculation of the dispersional and orientational interaction between acetone molecules in a monolayer Φ_{ii} gives 1.9 kcal/mole (here the orientational contribution amounts to ~ 50% [14]) and this is in agreement with the experimental value $Q_{max} - Q_0 = 1.5$ kcal/mole.

For acetic acid $Q_0 = 9.4$ kcal/mole and a theoretical calculation of the energy of the dispersional and inductional interaction $\bar{\Phi}_0'$ for isolated acetic acid molecules (monomer) by means of previously given formulas [14, 21] gave 7.5 kcal/mole.* So, the initial heat of adsorption of acetic acid is about 2 kcal/mole higher than the theoretically calculated adsorption energy of an isolated molecule (monomer). Just as in the case of alcohols, such a marked difference may be explained by adsorbate interaction in the monolayer resulting from the formation of hydrogen bonds at very small surface coverages for acetic acid this is still more probable, because in the vapor phase it is partially associated [3]. If acetic acid forms dimers on the surface, then one hydrogen bond (~7 kcal/mole [22]) is formed per monomer molecule. But the dispersion energy per acetic acid molecule entering a dimer is smaller than the adsorption energy of an isolated monomer, because in the adsorption of the dimer the plane of the

* In the calculation we used the values given in [7, 14] for the polarizability α and the diamagnetic susceptibility χ of the force centra CH_3, C, O, OH in the acetic acid molecule. The equilibrium distance of the molecule from the surface was determined from the van der Waals radii, as are also given in [2, 14, 15]. Since the thickness of the molecule decreases from the CH_3 group to the O atom, we assumed in this calculation that the plane of the molecule is inclined to the surface.

molecule is parallel to the surface at the distance determined by the van der Waals radius of the biggest group, namely, that of the CH_3 group. In the adsorption of acetic acid dimers from the gas phase the dispersional interaction amounts to 6.0 kcal/mole. But if monomers are adsorbed from the gas phase under formation of dimers on the surface, the adsorption energy amounts to 13 kcal/mole. Values for the constant of acetic acid association to dimers in the gas phase are given in the paper [3]. Although the degree of association on the surface is now known, it may be assumed that near completion of a monolayer where as yet no second layer is formed to a noticeable extent, that is, near Q_{max}, the acetic acid molecules on the surface are completely associated. The maximum in the heat of adsorption for acetic acid corresponds to an equilibrium pressure p = 2.3 mm Hg. Upon using the association constant $K = 1.73\ mm^{-1}$ at 20°, as is calculated from the data in [3], we find that in the gas phase at this pressure 37% of the acetic acetic molecules are dimeric and 63% monomeric. Hence we get the adsorption energy: $-\Phi = 6.0 \cdot 0.37 + 13.0 \cdot 0.63 = 10.4$ kcal per mole, which is close to the value of $Q_{max} = 10.1$ kcal/mole.

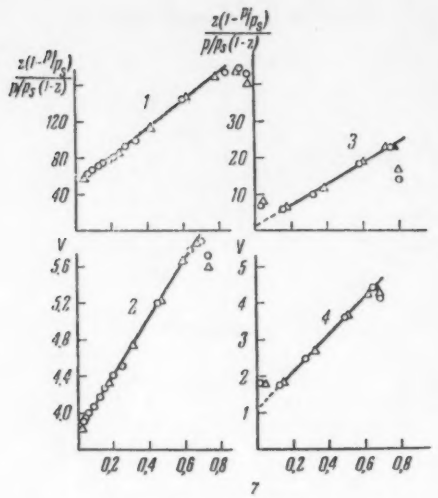

Fig. 4. Adsorption isotherms of diethyl ether (1,2) and acetone vapors (3, 4) on the graphitized thermal black T1, 3000° plotted in the coordinates of the equations for localized (1,3) and nonlocalized adsorption (2, 4).

From the considerations above it is evident that a comparison of the heats of adsorption Q_a with theoretically calculated values of the adsorption energy $-\Phi$ allows one to explain the sequence in which these heats vary from one class of substances to another at various coverages of the graphite surface. In all cases a great difference between Q_a and $-\Phi$ points to association of the adsorbate molecules by hydrogen bonds.

Energy, Free Energy and Entropy of Adsorption

From the isotherms and the differential heats of adsorption we calculated, just as we have done previously [7, 8, 11, 12] the differential changes in the free energy $\Delta\mu = RT \ln p/p_s$, energy $\frac{\partial \Delta U}{\partial \alpha} = -(Q_a - L)$ and adsorption entropy $\frac{\partial \Delta S}{\partial \alpha} = \frac{1}{T}\left(\frac{\partial \Delta U}{\partial \Delta} - \Delta\mu\right)$ for the transfer of diethyl ether and acetone from their standard state (liquid) to the adsorbed layer (Fig. 6).

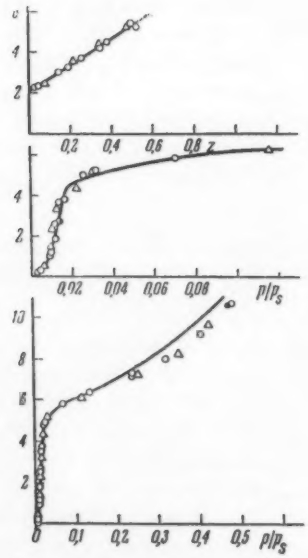

Fig. 5. Adsorption isotherm of acetic acid vapor on the graphitized thermal black T1, 3000°. Above, plotted in the coordinates of the equation for nonlocalized adsorption; in the middle and below, the curve calculated from the said equation; points designate experimental values.

It is evident that the energy curves for diethyl ether and acetone have a similar shape. At small surface coverages the entropy change is positive and this may result either from configurational entropy (localized adsorption) or from mobility of the molecules along the surface (nonlocalized adsorption). Upon approaching a complete monolayer the entropy change decreases and upon passing to a second layer it rises again.

At the right in Fig. 6 the mean molar entropy change calculated as $\Delta\overline{S}_m = \frac{1}{\alpha}\int_0^{\alpha} \frac{\partial \Delta S}{\partial \alpha} d\alpha$ is plotted versus the amount adsorbed. As this amount is raised, the state of the adsorbed layer approaches that of the liquid.

Finally, in Table 4 are given the heats of condensation L and the standard (surface coverage $\theta = 0.5$) thermodynamic

TABLE 4. Standard Thermodynamic Characteristics for the Adsorption of Acetone and Diethyl Ether at 20° on the Graphitized Carbon Black

Adsorbate	L kcal/mole	Q_a^0, kcal/mole	ΔU^0, kcal/mole	$\Delta\mu^0$, kcal/mole	ΔS^0, kcal/mole	$\Delta\bar{S}_m$, kcal/mole
Diethyl ether	6.4	9.7	−3.3	−2.9	−1.3	1.7
Acetone	7.5	8.9	−1.4	−1.7	1.0	3.8

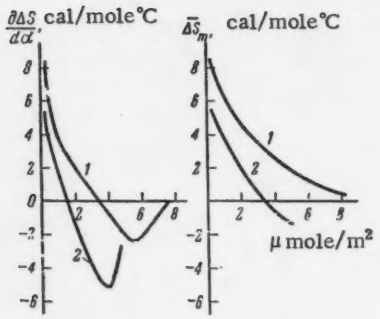

Fig. 6. Plots of the differential (left) and mean molar (right) adsorption entropy for the transfer of acetone (1) and diethyl ether (2) from the liquid to the adsorbed state on the graphitized thermal black T1, 3000°.

characteristics: the differential heats Q_a^0, the differential energies and free energies ΔU^0, $\Delta\mu^0$ and entropies of adsorption ΔS^0 and also the mean molar adsorption entropy $\Delta\bar{S}_m$.

The authors express their gratitude to Z. S. Kraits for providing the purified liquids.

SUMMARY

1. In a calorimeter with constant heat exchange we have measured isotherms and differential heats of adsorption of acetone, diethyl ether and acetic acid on a graphitized thermal black. At the start the isotherms are concave and the differential heats when plotted versus the amount adsorbed pass through a maximum.

2. The mutual interaction between these adsorbates in an adsorbed layer increases in the sequence from diethyl ether to acetone and acetic acid: this interaction originates from dispersional and electrostatic forces and in the case of acetic acid also from hydrogen bonds leading to the formation of dimers on the surface.

3. The theoretically calculated energies of the adsorption forces are in agreement with the heats of adsorption and give the right sequence for the various adsorbates.

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INVESTIGATION OF THE REACTION OF ELECTROPHILIC SUBSTITUENTS ON OLEFINIC CARBON ATOMS

2. REACTION OF TRANS- AND CIS-β-CHLOROVINYL MERCURY CHLORIDE WITH IODINE IN THE PRESENCE OF CADMIUM IODIDE IN ABSOLUTE METHANOL

I. P. Beletskaya, O. A. Reutov, and V. I. Karpov

M. V. Lomonosov Moscow State University

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No. 12, pp. 2125-2128, December, 1961
Original article submitted May 19, 1961

In the previous communication [1] the reaction of compounds with iodine in excess cadmium iodide in 85% aqueous dioxane was described. In this work data are given for studying the kinetics of this reaction and also the reaction of the cis-isomer in absolute methanol.

$$Cl—CH=CH—HgCl+I_2(CdI_2) \xrightarrow{CH_3OH} Cl—CH=CH—I+HgCl(CdI_2)$$

The kinetics were studied spectrophotometrically on an SF-4 apparatus with a thermostatted cell. The reaction was carried out between equimolar amounts of reagents with concentrations equal to $2\cdot10^{-5}$ and $8\cdot10^{-5}$ M/l and a cadmium iodide concentration of $2.1\cdot10^{-4}$ and $8.4\cdot10^{-4}$ M/l, respectively. The concentration interval of reagents used in methanol was different from that used earlier [1], since at concentrations of $1\cdot10^{-3}$ M/l at 20° in this solvent the reaction took place instantaneously. The iodine solution obeyed the Lambert-Beer law in the concentrations used. The relation of optical density to iodine concentration in cadmium iodide solutions in absolute methanol is given in Fig. 1. When lower concentrations of iodine and cadmium iodide ($2\cdot10^{-4}$ and $8\cdot10^{-4}$ M/l) were used in absolute methanol the relation between optical density and concentration was not linear. This fact, apparently, is caused by competition between two complex formers; methanol and cadmium iodide. This agrees with data that iodine solutions in methanol at these concentrations do not satisfy the requirements of the Beer-Lambert law.

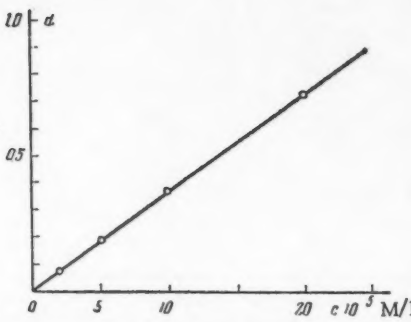

Fig. 1. Relation of optical density to concentration of iodine in methanol in the presence of cadmium iodide.

EXPERIMENTAL

To a thermostatted solution of chlorovinyl mercury chloride in absolute methanol [2] was added a thermostatted solution of iodine and cadmium iodide in alcohol. The experimental temperature was maintained precisely ± 0.05°. The time of adding the second component was taken as the start of reaction. A fixed volume of reaction mixture was placed in the thermostatted cell and the change of optical density at wavelength λ 410 mμ was followed on the SF-4 instrument at fixed time intervals. In work using solutions of different concentrations, which was required by variations in reaction temperature, cells of different lengths were used to obtain the optimum interval of changing optical density: when $C_0RHgX = 2\cdot10^{-5}$ M/l; l = 100 mm; d_0 = 0.700; when $C_0RHgX = 8\cdot10^{-5}$ M/l; l = 10 mm; d_0 = 0.300.

In Table 1 are given the experimental data obtained for changing optical densities with time at different initial concentrations at the various reaction temperatures.

A graph with the coordinates $\frac{d_0 - d}{d} - \tau$ showed convergence of the second order constants for the reaction cited and their changes with temperature variations (Figs. 2, 3).

From the graph was found the value for the half-life period for both cases and constants were computed from them $k_2 = \frac{1}{c_0 \cdot \tau_{1/2}}$ (Table 2).

The reaction rate constants, their logarithms, the corresponding absolute temperature, and values of their reciprocals, are given in Table 3.

From this data in Table 3 graphs of the function of the logarithm of the constant vs. reciprocal temperature were constructed for the cis- and trans-isomers (Fig. 4), from which parameters for the Arrhenius equation were found: trans-β-chlorovinyl mercury chloride, E = 11.70 kcal/M, log A = 10.40; entropy of activation equals − 11.0 E. U. at 25°; cis-β-chlorovinyl mercury chloride, E = 11.40 kcal/M; log A = 10.30, entropy of activation equals − 11.6 E. U. at 25°.

TABLE 1.

Trans-β-chlorovinyl mercury chloride						Cis-β-chlorovinyl mercury chloride					
10° $c_0 RHgX = c_0 I_2 = 8 \cdot 10^{-5}$ M/l $c_0 CdI_2 = 8{,}4 \cdot 10^{-4}$ M/l		15° $c_0 RHgX = c_0 I_2 = 8 \cdot 10^{-5}$ M/l $c_0 CdI_2 = 8{,}4 \cdot 10^{-4}$ M/l		20° $c_0 RHgX = c_0 I_2 = 2 \cdot 10^{-5}$ M/l $c_0 CdI_2 = 2{,}1 \cdot 10^{-4}$ M/l		10° $c_0 RHgX = c_0 I_2 = 8 \cdot 10^{-5}$ M/l $c_0 CdI_2 = 8{,}4 \cdot 10^{-4}$ M/l		15° $c_0 CdI_2 = 8{,}4 \cdot 10^{-4}$ M/l $c_0 RHgX = c_0 I_2 = 8 \cdot 10^{-5}$ M/l		20° $c_0 CdI_2 = 2{,}1 \cdot 10^{-4}$ M/l $c_0 RHgX = c_0 I_2 = 2 \cdot 10^{-5}$ M/l	
t, sec	d	t, sec	d	t, sec	d	t, sec	d	t, sec	d	t, sec	d
0	0,300	0	0,300	0	0,700	0	0,300	0	0,300	0	0,700
80	0,251	70	0,248	60	0,650	55	0,263	60	0,250	60	0,635
120	0,236	90	0,232	120	0,610	90	0,242	90	0,230	120	0,600
150	0,228	130	0,210	180	0,580	120	0,227	120	0,208	180	0,560
180	0,214	180	0,190	240	0,555	150	0,214	150	0,193	240	0,526
240	0,195	240	0,172	270	0,539	180	0,200	180	0,183	300	0,496
300	0,180	270	0,161	300	0,520	240	0,183	240	0,158	420	0,446
360	0,166	330	0,147	360	0,495	300	0,165	300	0,143	510	0,412
420	0,154	360	0,137	420	0,468	360	0,153	360	0,130	540	0,400
480	0,145	420	0,129	480	0,455	420	0,140	420	0,118	600	0,385
540	0,136	480	0,122	540	0,438	480	0,131	480	0,108	660	0,367
600	0,129	510	0,115	600	0,415	540	0,122			720	0,355
660	0,122	560	0,109	660	0,400	600	0,114			780	0,340
720	0,116			720	0,385	660	0,108			840	0,330
				780	0,373	720	0,102			900	0,312
				840	0,358	780	0,096			1020	0,295
				930	0,340	840	0,091			1080	0,283
				1200	0,298	900	0,087			1200	0,266

TABLE 2.

Trans-β-chlorovinyl mercury chloride				Cis-β-chlorovinyl mercury chloride			
$C_0 RHgX \cdot 10^5$	temperature, °C	$\tau_{\frac{1}{2}}$, sec	k_2 1/M · sec	$C_0 RHgX \cdot 10^5$	temperature, °C	$\tau_{\frac{1}{2}}$, sec	k_2 1/M · sec
8	10	450	27.5	8	10	370	33.8
8	15	310	40.4	8	15	275	45.5
2	20	885	56.5	2	20	745	67.6

The stereochemistry of the reaction of trans- and cis-β-chlorovinyl mercury chloride with iodine in the presence of cadmium iodide in absolute methanol was studied.

To a solution of 3 g (0.0101 M) of trans-β-chlorovinyl mercury chloride in 50 ml of absolute methanol was added a solution of 2.6 g (0.0102 M) of iodine and 36.6 g (0.1 M) of CdI_2 in 100 ml of absolute methanol. The

iodine color was lost immediately. The methanol was carefully distilled. The residue formed was washed on the filter with petroleum ether (10 ml portions) several times. After distilling the petroleum ether the residue was distilled on a Wood's metal bath at 110-111°. Trans-1,2-chloroiodoethylene (1.15 g; 61% of theor.) with $n^{15}D$ 1.5718 was obtained.

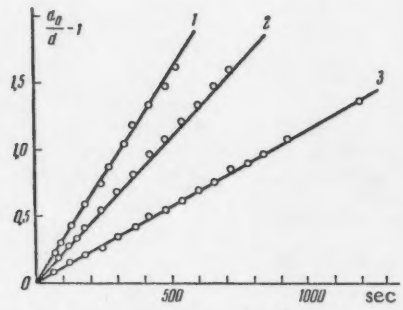

Fig. 2. The function $\frac{a_0-a}{a} = f(\tau)$ for trans-β-chlorovinyl mercury chloride at different temperatures: 1) 15°; 2) 10°; 3) 20°.

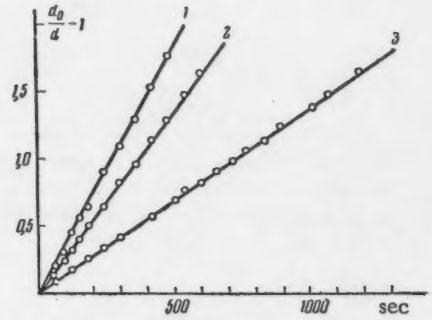

Fig. 3. The function $\frac{a_0-a}{a_0} = f(\tau)$ for cis-β-chlorovinyl mercury chloride at different temperatures: 1) 15°; 2) 10°; 3) 20°.

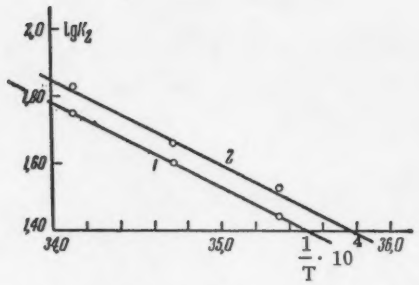

Fig. 4. Function of logarithm of the second-order rate constant vs. reciprocal of the absolute temperature for two isomers: 1) trans-β-chlorovinyl mercury chloride; 2) cis-β-chlorovinyl mercury chloride.

TABLE 3.

Trans-β-chlorovinyl mercury chloride

k_2, 1/M·sec	log k_2	T	$1/T\cdot 10^4$
56.5	1.7520	293	34.13
40.3	1.6055	288	34.72
27.8	1.4440	283	35.34

Cis-β-chlorovinyl mercury chloride

k_2, 1/M·sec	log k_2	T	$1/T\cdot 10^4$
67.6	1.8299	293	34.13
45.5	1.6580	288	34.72
33.8	1.5289	283	35.34

Under similar conditions 1.18 g (62.8% of theor.) of cis-β-1,2-chloroiodoethylene boiling at 114-115.5° with $n^{15}D$ 1.5815 was obtained from 3 g of cis-β-chlorovinyl mercury chloride. Literature data [3]: trans-chloroiodoethylene – b. p. 113-114°; $n^{15}D$ 1.5715; cis-chloroiodoethylene – b. p. 116-117°; $n^{15}D$ 1.5828.

Thus, the reaction of β-chlorovinyl mercury chloride with iodine in the presence of excess cadmium iodide in methanol occurs according to the Nesmeyanov-Borisov rule [4] with strict retention of geometric configuration.

SUMMARY

1. The reaction of cis- and trans-β-chlorovinyl mercury chloride with iodine in an excess of cadmium chloride in absolute methanol was studied.

2. Rate constants were determined for the second order reaction at various temperatures and the Arrhenius equation parameters were calculated.

3. The stereochemistry of the process was studied. Under the conditions used the reaction occurs with strict retention of geometric configuration.

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INVESTIGATION OF THE REACTION OF ELECTROPHILIC SUBSTITUENTS ON OLEFINIC CARBON ATOMS

3. REACTION OF TRANS- AND CIS-β-CHLOROVINYL MERCURY CHLORIDE WITH IODINE IN THE PRESENCE OF CADMIUM IODIDE IN DIMETHYLFORMAMIDE

I. P. Beletskaya, O. A. Reutov, and V. I. Karpov

M. V. Lomonosov Moscow State University
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Original article submitted May 19, 1961

In the preceding articles the reaction of compounds with iodine in excess cadmium iodide in 85% aqueous dioxane [1] as well as the reaction of trans- and cis-β-chlorovinyl mercury chloride in absolute methanol [2] were described. It was shown that the reaction has overall second order kinetics. The reaction of the electrophilic substituent HgX with I under these conditions occurs with strict retention of geometric configuration; trans-chloroiodoethylene is obtained from trans-β-chlorovinyl mercury chloride in dioxane; in absolute methanol the trans isomer gives trans-chloroiodoethylene and the cis isomer gives cis-chloroiodoethylene without admixed second isomer. Comparison of the second-order rate constants in 85% dioxane and in absolute methanol shows a marked rise in rate of reaction (75 times) in absolute methanol (at 20°).

In this study data for studying this reaction in dimethylformamide were gathered. The reaction kinetics were studied

$$Cl—CH=CH—HgCl+I_2\,(CdI_2) \xrightarrow{HCON(CH_3)_2} ClCH=CHI+HgClI\,(CdI_2)$$

by photocolorimetric methods. The reaction of trans- and cis- isomers was conducted with equivalent ratios of reagents with concentrations equal to $1\cdot10^{-3}$ M/l and the concentration of CdI_2 equal to $1\cdot10^{-2}$ M/l. The reaction rate was measured at 15, 25, and 35°. Measurements were made on an FÉK apparatus with a green filter (trans isomer) and on the FEKN-57(No. 3 filter, cell 50.08, cis isomer) instrument. The linear relation between optical density and iodine concentration in cadmium iodide solutions in dimethylformamide is shown on Fig. 1. Dimethylformamide was purified by method [3].

The experimental data for changes in optical density d with time for trans- and cis- β-chlorovinyl mercury chloride at different temperatures and constant reagent concentrations are summarized in Table 1.

From the data in Table 1 graphs with coordinates $d_0/d-1-t$, which corresponds to $c_0/c-1-t$ for the trans- (Fig. 2) and cis isomers (Fig. 3) were constructed. The results obtained lead to a second order kinetic mechanism. Values for the half-life period of reaction were found from the graph and from these the second-order reaction rate constant $k_2=\frac{1}{c_0\cdot\tau_{1/2}}$ was computed for all cases.

The actual value of the reaction rate constants, their logarithms, absolute temperatures and their reciprocals are given in Table 2.

From the data in Table 2 a graphic relation between the logarithm of K_2 as a function of the reciprocal of temperature for trans- (Fig. 4) and cis- (Fig. 5) isomers were constructed; the parameters of the Arrhenius equation and entropy of activation were calculated from them: trans-β-chlorovinyl mercury chloride: E = 10.10 kcal/M; log A = 7.2; $\Delta S_{act} = -25.8$ E. U. at 25°; cis-β-chlorovinyl mercury chloride: E = 9.50 kcal/M; log A = 6.8; $\Delta S_{act} = -27.6$ E. U. at 25°.

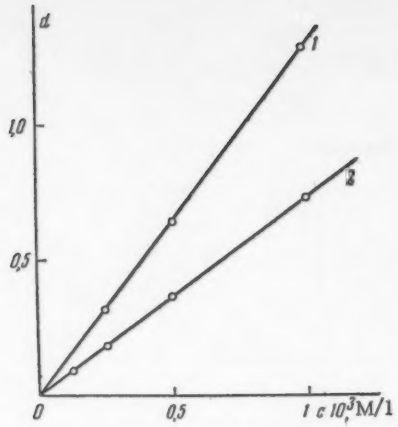

Fig. 1. Relation of optical density to iodine concentration in dimethylformamide in the presence of cadmium iodide: 1) on FÉK apparatus; 2) on FÉKN-57 apparatus.

TABLE 1.

c_0 RHgX = $c_0 I_2$ = 1·10⁻³ M/l				c_0 CdI_2 = 1·10⁻² M/l	
15°		25°		35°	
t, sec	d	t, sec	d	t, sec	d
Trans-β-chlorovinyl mercury chloride					
0	1,280	0	1,280	0	1,280
240	1,190	185	1,140	100	1,155
720	1,020	535	0,950	165	1,080
900	0,950	720	0,875	290	0,980
1680	0,805	1080	0,760	395	0,882
1800	0,770	1440	0,665	505	0,805
2400	0,680	1652	0,635	755	0,685
3000	0,615	1810	0,595	975	0,600
3600	0,575	2195	0,560	1140	0,565
Cis-β-chlorovinyl mercury chloride					
0	0,725	0	0,725	0	0,725
180	0,670	140	0,640	200	0,585
300	0,650	270	0,575	360	0,520
480	0,610	540	0,545	480	0,465
600	0,590	780	0,485	600	0,425
900	0,535	1000	0,440	780	0,390
1200	0,495	1220	0,400	900	0,355
1500	0,455	1480	0,370	1200	0,310
1800	0,430	1800	0,340	1500	0,270
2100	0,400	2000	0,315	1800	0,240
2400	0,375	2300	0,295		
2700	0,350	2460	0,280		
3000	0,330	3000	0,250		

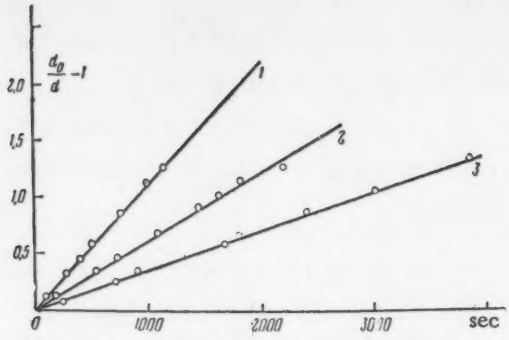

Fig. 2. Graph of the function $\frac{d_0-d}{d}=f(\tau)$ at different temperatures for trans-β-chlorovinyl mercury chloride at: 1) 35°; 2) 25°; 3) 15°.

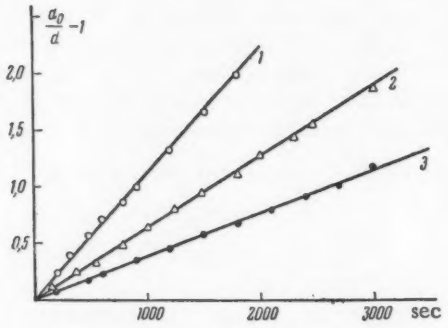

Fig. 3. Graph of the function $\frac{d_0-d}{d}=f(\tau)$ at different temperatures for cis-β-chlorovinyl mercury chloride: 1) 35°; 2) 25°; 3) 15°.

Owing to the high boiling point of dimethylformamide (153°) it seemed unsuitable to carryout studies of stereochemical processes in that solvent.

For comparison of the kinetic data obtained studying the reaction of isomeric β-chlorovinyl mercury chlorides with iodine in the presence of excess cadmium iodide in different solvents the second-order reaction rate constants at 15°, the parameters of the Arrhenius equation, and the entropy of activation are given in Table 3.

The reaction rate in the solvents for both isomers is arranged in the following order: methanol > 85% aqueous dioxane > dimethylformamide which agrees with the previously obtained values for this same reaction with benzyl mercury chloride [4].

It is interesting to note that by changing the reaction medium the change in reaction rate depends mainly on the entropy factors. In all of the solvents studied the cis isomer has a higher reactivity than the trans isomer.

TABLE 2.

Trans-β-chlorovinyl mercury chloride				Cis-β-chlorovinyl mercury chloride		
c_0	$c_{RHgX} = c_{I_2} = 1 \cdot 10^{-3}$ M/l $c_{CdI_2} = 1 \cdot 10^{-2}$ M/l			$c_{RHgX} = c_{I_2} = 1 \cdot 10^{-3}$ M/l $c_{CdI_2} = 1 \cdot 10^{-2}$ M/l		
T	288	298	308	288	298	308
$\frac{1}{T} \cdot 10^4$	34,7	33,6	32,5	34,7	33,6	32,5
$\tau_{1/2}$, sec	2820	1680	912	2560	1560	880
k_2, 1/M·sec	0,356	0,594	1,096	0,391	0,640	1,14
log k_2	—0,449	—0,226	0,040	—0,408	—0,194	0,056

TABLE 3.

Solvent	k_2 1/M·sec at 15°	E, kcal/M	log A	ΔS_{act} at 25°
Trans-β-chlorovinyl mercury chloride				
Methanol	40.40	11.7	10.4	−11.0
85% Aqueous dioxane	0.516	13.6	10.0	−12.8
Dimethylformamide	0.356	10.1	7.2	−25.8
Cis-β-chlorovinyl mercury chloride				
Methanol	45.50	11.4	10.3	−11.6
Dimethylformamide	0.319	9.5	6.8	−27.6

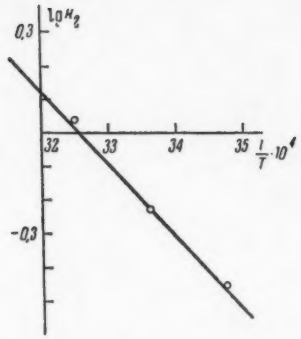

Fig. 4. Relation of logarithm of the second-order rate constant to reciprocal of the absolute temperature for trans-β-chlorovinyl mercury chloride.

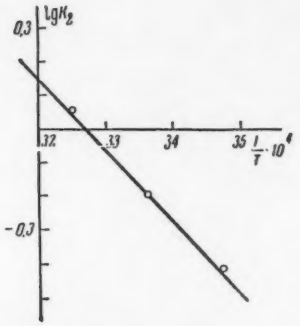

Fig. 5. Relation of logarithm of the second-order rate constant to reciprocal of the absolute temperature for cis-β-chlorovinyl mercury chloride.

SUMMARY

1. The reaction of cis- and trans-β-chlorovinyl mercury chloride with iodine in the presence of excess cadmium iodide in dimethylformamide was studied.

2. Constants for the second-order rate constant at different temperatures were determined.

3. The parameters of the Arrhenius equation were found.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

THE DEPENDENCE OF THE FREQUENCY OF VIBRATION OF THE Ge-C BOND IN THE SPECTRA OF ALKYLGERMANES ON THE NATURE OF THE SUBSTITUENTS

L. A. Leites, Yu. P. Egorov, G. Ya. Zueva, and

V. A. Ponomarenko

The N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR
and the P. N. Lebedev Physical Institute, Academy of Sciences, USSR
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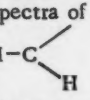
The similarity of physical properties of the germanium and silicon atoms suggests that structurally similar organic compounds of these elements possess similar physical and chemical properties, although each of these classes of organo metallic compounds also possesses its own peculiarities (see for example [1]).

The purpose of this work was to trace the common features in the vibration spectra of the alkylgermanes and to illustrate the interaction of tetra-alkylgermanes with aluminum halides and bromine.

An examination of the Raman spectra of the organo germanium compounds which are given in Table 1 (these were obtained by us [2-4] or extracted from the literature [5-8]) discloses that the germanium atom to a greater degree than the silicon atom [9] manifests "barrier" properties, making it possible to find the characteristic frequencies of the groups: CH_3, C_2H_5, n-C_3H_7, $-CH=CH_2$ and $-CH-CH=CH_2$ which are joined to the germanium atom (Table 2); these may be used for analytical purposes. It is seen in Table 2 that the frequencies of these groups in the Raman spectra of organo germanium compounds differ little from these same group frequencies in the Raman spectra of the silicon compounds [10]. The only exception is the frequency of the angular deformation vibration of  (where M −Si, Ge) in the 1270-1140 cm^{-1} region. The exchange of germanium for silicon lowers this frequency by 10-15 cm^{-1}.

The "barrier" character of the germanium atom is also clearly evident in the infrared spectra of the alkylgermanes (see Table 1 and Figs. 1-10). Thus in the infrared spectra of $(C_2H_4)_4Ge$ absorption bands are observed at 1460, 1425, 1378, 1234, 1019, 968 and 700 cm^{-1}. These bands are present in the infrared spectra of all organogermanium compounds which contain an ethyl group. The n-C_3H_7 radical attached to germanium is characterized in the infrared by absorption bands at 1465, 1428, 1384, 1340, 1215, 1070, 1005 and 645 cm^{-1}; CH_3 by absorption bands at ~1240, 1410 and 800 cm^{-1} (in agreement with the data of [6] and [11]). If there are several different radicals in the molecule the region from 1460-1370 and 1250-1200 cm^{-1} becomes uncharacteristic, since the absorption bands of the different radicals overlap one another. In this case one may judge of the presence of an ethyl group on germanium by the bands at ~1020, 960 and 700 cm^{-1}, and of the presence of the n-propyl group by the bands at 1335, 1070, 1005 and 645 cm^{-1}.

An examination of the spectra of the methyl- ethylgermanes shows that one may follow the change of the skeletal frequencies as a function of the change of symmetry of the molecule according to the scheme

$$\underset{(CH_3)_4Ge}{T_d} \longrightarrow \underset{(CH_3)_3GeC_2H_5}{C_{3v}} \longrightarrow \underset{(CH_3)_2Ge(C_2H_5)_2}{C_{2v}} \longleftarrow \underset{CH_3Ge(C_2H_5)_3}{C_{3v}} \longleftarrow \underset{Ge(C_2H_5)_4}{T_d}$$

(Table 3), in a way analogous to that which we did for the methyl allyl germanes [4]. The spectra of these series and also of the other tetraalkylgermanes which have been investigated allows one to observe that the presence of two or more identical substituents on a germanium atom causes the appearance in the spectrum of a stable, unsymmetrical, skeletal valence vibration frequency (of type F_2, E, or B in accordance with the symmetry of the molecule)

TABLE 1

The Raman* and Infra-red** Spectra of Some Alkylgermanes

$CH_3Ge(n\text{-}C_3H_7)_3$		$n\text{-}C_3H_7Ge(C_2H_5)_3$	$ClGe(C_2H_5)_3$		$BrGe(C_2H_5)_3$	$Ge(C_2H_5)_4$		$Ge(n\text{-}C_3H_7)_4$	
Raman	Infra-red	Raman	Raman	Infra-red	Raman	Raman	Infra-red	Raman	Infra-red
190 (2 b)			155 (3 b)		147 (3sp)	153 (3b)		150 (2)	
238 (2b)		242 (0)			243 (5)	252 (0)		247 (2 b)	
269 (0b)			265 (0)						
297 (3b)		285 (2 b)	290 (2)		294 (1)	286 (4 b)		287 (1 b)	
		317 (1)	317 (1)		332 (0)	332 (1b)		299 (1)	
								326 (0)	
			367 (5b)					375 (0)	
403 (1 b)								405 (1)	
495 (1 b)									
		536 (10 b)	544 (10)	548 (m)	543 (10 b)	532 (10)			
553 (7 b)	560 (w)							556 (6 b)	557 (m)
		573 (7b)				572 (8 b)	575 (s)		
584 (10)	588 (s)		591 (5 b)	593 (s)	591 (6 b)				
639 (6 b)	643 (m)	639 (2 b)						618 (5)	
								641 (6b)	643 (m)
	690 (m)						700 (s)		693 (s)
	716 (w)			710 (s)					725 (w)
801 (0)	778 (s)	802 (1)						802 (7sp)	806 (m)
	809 (m)								
									854 (w)
	852 (w)			851 (w)				879 (1)	882 (w)
876 (3 sp)	875 (w)	895 (1)						896 (6)	
892 (3 sp)									
968 (0)		971 (2)	978 (2)	969 (m)	980 (2 b)	976 (5)	968 (m)		1007 (s)
1010 (1)	1003 (s)	1017 (1)	1013 (1)		1016 (2 b)			1035 (10)	1032 (w)
1031 (5)		1029 (2 b)	1027 (1 b)	1028 (m)	1032 (2 b)	1025 (3 b)	1019 (m)	1072 (3 b)	1070 (s)
1067 (2 b)	1072 (s)	1070 (1)							
		1105 (0)	1107 (1)		1107 (2)	1104 (1)			
1129 (1 b)		1134 (0)	1137 (1)		1139 (0)	1138 (1 b)		1165 (1)	1172 (w)
								1192 (8)	1201 (w)
1190 (8)		1189 (3)						1210 (2)	1215 (m)
1211 (1)	1212 (w)	1220 (5)	1227 (5)	1230 (w)	1225 (6 b)	1223 (8)			
1236 (2 b)	1238 (m)						1234 (m)		
								1268 (1)	
1295 (2b)		1286 (0)				1299 (1)		1299 (1)	
								1331 (2)	1342 (m)
1329 ( )	1331 (m)	1325 (1)				1328 (2)		1386 (0)	1384 (m)
	1375 (m)	1379 (1)	1380 (1)	1384 (m)	1382 (1)	1381 (2)	1378 (m)	1420 (2)	1428 (m)
1419 (3)	1418 (m)	1425 (2)	1425 (2)	1424 (m)	1423 (2)	1430 (3)	1426 (m)	1449 (8 b)	
1452 (8 b)									1465 (s)
	1459 (s)	1460 (4)	1460 (4)	1462 (m)	1462 (5 b)	1463 (7)	1461 (m)		
	2810 (w)			2825 (w)			2830 (w)	2818 (0)	2812 (w)
2865 (9)	2868 (v.s)	2873 (8)	2876 (6sp)	2884 (s)	2877 (9)	2874 (9)	2876 (s)	2661 (9)	2858 (s)
2900 (10)		2903 (10)	2908 (5)	2908 (s)	2903 (9)	2905 (10)	2910 (v.s)	2901 (10)	
2933 (6)	2923 (v.s)	2930 (3)	2936 (5)	2935 (s)	2937 (9)	2930 (7)		2935 (8)	2926 (v.s)
2961 (8)	2959 (v.s)	2956 (4)	2963 (4)	2960 (s)	2960 (7 b)	2954 (8)	2954 (v.s)	2964 (9)	2959 (v.s)

* The Raman spectra were obtained on an ISP-51 instrument with a central chamber; the 4358 A mercury line was used for excitation. Intensities are cited on a 10-point visual scale.

** The infra-red spectra were run on a double beam UR-10 spectrophotometer in the 400-1800 and 2800-3100 cm^{-1} regions. The thickness of the absorbing layer was 0.02 mm. The symbols are: s-strong; m-medium; w-weak; b-broad; sp-sharp; d-double; v-very.

Table 1 (cont.).

$(CH_3)_3Ge{\cdot}C_3H_5$		$(CH_3)_3Ge{\cdot}n\text{-}C_3H_7$		$(CH_3)_2Ge(C_3H_5)_2$		$(CH_3)_2Ge(n\text{-}C_3H_7)_2$		$(CH_3)_2Ge(C_6H_5)_2$		$(CH_3)Ge(C_3H_5)_3$	
Raman	Infra-red	Raman	Infra-red	Raman	Infra-red	Raman	Infra-red	Raman	Infra-red	Raman	Infra-red
195 (7b)		194 (8b)		190 (5b)		187 (4 b)		180 (3)		174 (3b)	
								206 (2)			
								233 (3)			
		260 (2)		275 (2 b)		249 (1)				263 (1)	
		308 (3)		305 (1)		307 (3 b)		290 (3)		287 (2 b)	
290 (3)										319 (0)	
						384 (1b)					
	490 (w)		487 (w)						467 (s)		
				544 (10)						536 (10)	
552 (10)	555 (w)	550 (5)			550 (w)	552 (5)	560 (w)				
		567 (10)	572 (m)	574 (3)		572 (7)				573 (8)	
587 (6)				588 (6)	585 (s)	586 (1)		580 (8)	587 (m)	592 (8)	580 (v. s)
600 (7)	595 (s)	600 (8)	600 (s)	600 (6)	595 (s)	601 (5)	597 (s , b)	601 (4 sp)	608 (m)		593 (s)
		643 (4)	645 (w)			646 (4b)	645 (m)	616 (3 sp)			
	675 (w)		673 (w)		685 (m)		685 (w)	669 (4)	677 (w)		675 (w)
					700 (m)				703 (s)		705 (s)
	765 (m)		753 (s)		746 (m)		738 (m)		732 (s)		
798 (3)			777 (w)		797 (s)	789 (0)	790 (m)		808 (s)		783 (s)
					807 (s)						
	819 (v. s)	827 (1)	820 (v. s)				814 (v. s)		826 (s)		
			850 (w)		849 (m)		848 (w)		849 (m)		852 (w)
	897 (w)	893 (1)				890 (2b)	886 (w)		908 (w)		
973 (1 b)	960 (m)			970 (2)	959 (m)		953 (w)	942 (3 sp)		973 (3)	965 (m)
		1005 (0)	1003 (m)				1002 (m)	999 (10)	998 (w)		
1025 (2b)	1018 (m)	1032 (2)		1020 (2)	1020 (s)	1031 (5)		1029 (4 sp)	1026 (w)	1020 (3 b)	1020 (s)
		1073 (1)	1068 (m)			1070 (2b)	1071 (m)	1088 (2)	1063 (w)		
				1105 (1)		1101 (1b)			1098 (m)		
1140 (1 b)		1136 (2 b)		1140 (3)		1133 (1b)					
				1166 (0)				1154 (2)	1154 (w)	1164 (0)	
		1190(4)				1188 (5)		1187 (1)	1183 (w)		
1224 (2)		1207 (1 b)		1220 (4)		1208 (0)	1212 (w)			1222 (5)	
	1235 (s)	1236 (2)	1235 (s)	1238 (3)	1242 (s)	1238 (4)	1242 (m)	1243 (1)	1242 (m)	1239 (2)	1239 (m)
1249 (4)		1245 (3)									
		1292 (1)		1296 (0)		1291 (1)	1287 (w)		1261 (w)		
									1302 (w)		
1327 (0)		1329 (1)	1330 (m)	1324 (1 b)		1331 (2)	1334 (m)		1333 (w)	1325 (0)	
	1376 (w)		1375 (w)		1376 (w)		1375 (m)	1389 (0)	1376 (w)	1382 (1 b)	1378 (m)
1420 (1 b)	1415 (w)	1415 (3b)	1415 (m)	1421 (2 b)	1424 (w)	1419 (3)	1415 (m)		1410 (w)	1427 (3)	1420 (m)
	1450 (w)	1449 (3 b)				1452 (5b)			1430 (s)		
1461 (2 b)	1460 (w)		1455 (m)	1460 (3 b)	1459 (m)		1456 (s)			1460 (4 b)	1460 (m)
									1486 (m)		
								1572 (1)			
								1583 (8)	1589 (w)		
									1643 (w)		
	2830 (w)		2815 (m)		2822 (m)		2807 (m)		2804 (w)		2822 (m)
	2854 (m)										
2878 (3)	2875 (s)	2867 (4)	2870 (m)	2873 (5sp)	2879 (s)	2864 (4)	2867 (v.s)			2875 (7)	2872 (s)
2910(10 b)	2910 (v.s)	2903 (9 b)	2910 (s)	2905 (10)	2903 (v.s)	2902 (10)	2900 (v.s)	2910 (3 b)	2909 (m)	2906 (10)	2901 (v.s)
2941 (1)	2930 (v.s)	2938 (3)	2924 (s)	2932 (2)		2932 (2)	2923 (v.s)			2928 (2)	
	2955 (v.s)		2960 (s)	2954 (2)	2955 (v.s)		2960 (v.s)			2951 (3)	2958 (v.s)
2977 (7 b)	2974 (s)	2975 (8)		2976 (4b)		2968 (4, d)		2979 (1 b)	2980 (m)	2975 (2)	
									2998 (m)		
									3017 (m)		
									3040 (s)		
								3075 (0)	3075 (s)		

which is characteristic for the given substituents and which does not depend on the form of the other radicals (for the CH_3 group this is at approximately 600 cm^{-1}, for the C_2H_5 group at 573 cm^{-1}, for the $-CH_2-CH=CH_2-$ 538 cm^{-1}) [4]. Atoms of chlorine or bromine on the germanium raise this frequency. One cannot follow the change of skeletal frequencies of the propylgermanes in this way since, because of the considerable volume of the propyl radicals, the molecules $(C_3H_7)_4Ge$ and $(C_3H_7)_3GeR$ do not belong to groups T and C_{3v} respectively, but possess lower symmetries.

TABLE 2. The Characteristic Frequencies of Some Groups

Group	Frequency in cm^{-1}		Group	Frequency in cm^{-1}	
	Si	Ge		Si	Ge
CH_3	~1250	~1240	$-CH=CH_2$	1272	1263
				1406	1400
				1594	1593
				3050	3040
C_2H_5	972	975	$CH_2-CH=CH_2$	410	400
	1015	1020		930	932
	1233	1220		990	990
	1462	1460		1155	1145
				1193	1195
n-C_3H_7	1030	1030		1300	1300
	1066	1070		1398	1397
	1200	1190		1630	1630
	1455	1450		3000	2996
				3078	3080

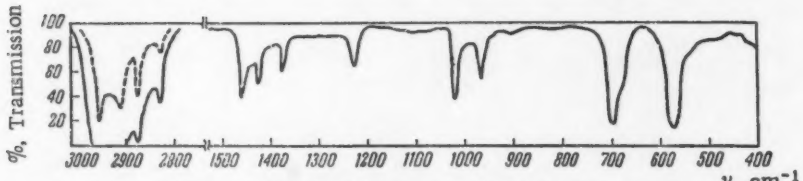


Fig. 1. The infrared spectrum of $(C_2H_5)_4Ge$.

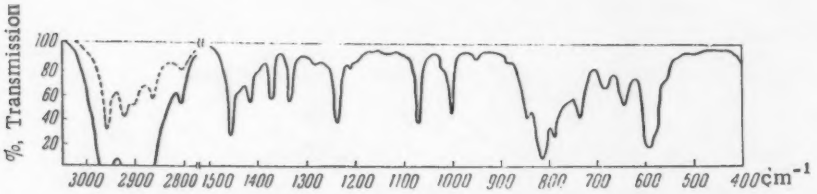


Fig. 2. The infrared spectrum of $(CH_3)_2Ge(n\text{-}C_3H_7)_2$.

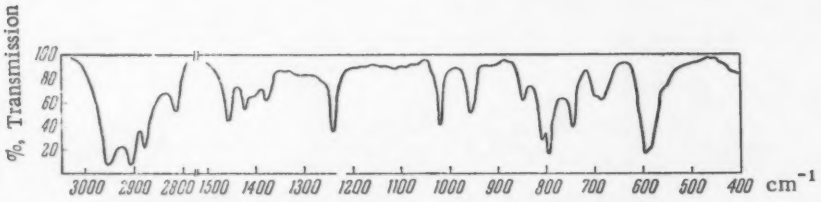


Fig. 3. The infrared spectrum of $(CH_3)_2Ge(C_2H_5)_2$.

An examination of the positions of the frequency of the fully symmetric valence vibration of the Ge-C bond*

* It is apparent from the literature data of [5-6], that the frequencies of the valence vibrations of the Ge-C bonds are to be found in the 500-650 cm^{-1} region. We elicited the frequencies, basing them on data of the intensities and polarizations of the lines. Where two lines were present in the spectrum of the molecule which corresponded to the symmetrical valence vibrations of the skeleton (symmetry type C_{3v} or C_{2v}), we selected the frequency of the more intense line for the reasons set forth in [12].

(ν_{Ge-C}) in the spectra of tetra-substituted germanes which are described in the literature [2-8] and of those given in the present work allows one to observe a dependence between this frequency and the effective electronegativity of the substituents on the germanium atom (Fig. 11), similar to that which was made by Egorov [12] for silicon compounds. This dependence is described by the formula:

$$\nu_{G-Ce} = \frac{43{,}325 \cdot 10^5}{8208 - \left(\sum e_i\right)^3}, \quad (1)$$

where Σe_i is the sum of the effective electronegativities (Eff. EN)* of the four substituents on the germanium atom. The analogous formula for ν_{Si-C} has the form

$$\nu_{Si-C} = \frac{1655}{\sqrt{15{,}77 - \sum e_i}}. \quad (2)$$

Attempts to describe the dependence of ν_{Ge-C} on the effective electronegativity of the substituents by a formula of type (2), that is, $\nu = \frac{a}{\sqrt{b - \sum e_i}}$ was unsuccessful. It turned out that a formula of the type

$$\nu_{Ge-C} = \frac{2079}{\sqrt{21{,}9 - \sum e_i}} \quad (3)$$

gives satisfactory agreement with experiment only when $\Sigma e_i > 8$. Formula (1), on the other hand, describes the entire curve. It should be observed that both formula (1) and formula (2) were selected in a purely empirical fashion. Another kind of formula which would be useable for both ν_{Si-C} and ν_{Ge-C} is not excluded.

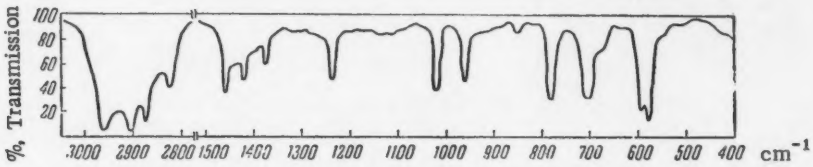


Fig. 4. The infrared spectrum of $CH_3Ge(C_2H_5)_3$.

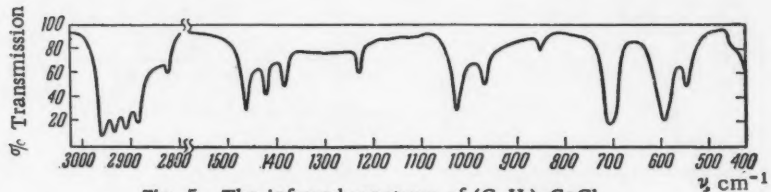


Fig. 5. The infrared spectrum of $(C_2H_5)_3GeCl$.

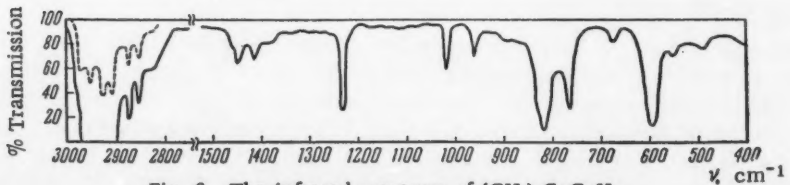


Fig. 6. The infrared spectrum of $(CH_3)_3GeC_2H_5$.

* We drew attention to this unfortunate term "effective electronegativity" in [12]. We use it only on the strength of established tradition.

In the construction of the graphical dpendence of ν_{Ge-C} we made use of the values from the spectra of the molecules of methylchloro- and methylbromo- derivatives of germanium, taking the effective electronegativity of chlorine as 3 and of bromine as 2.85 (according to Pauling), and of the methyl group as 2 (as was done in [12]). Starting with the graph and the experimental values of ν_{Ge-C} for molecules with other radicals attached to germanium, we calculated the magnitude of the effective electronegativities of these radicals (Table 4).

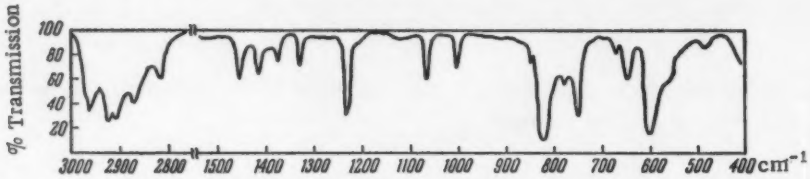


Fig. 7. The infrared spectrum of $(CHE)_3GeC_3H_7$.

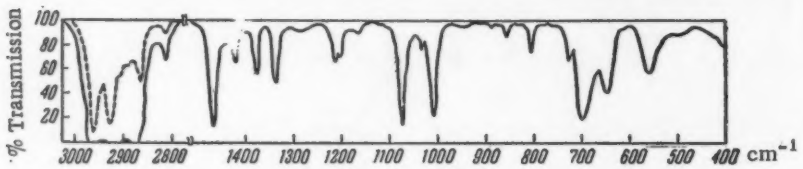


Fig. 8. The infrared spectrum of $Ge(n\text{-}C_3H_7)_4$.

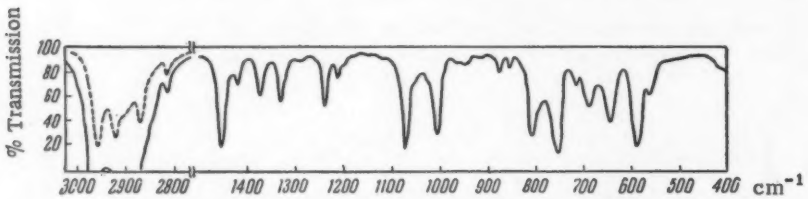


Fig. 9. The infrared spectrum of $(CH_3)Ge(n\text{-}C_3H_7)_3$.

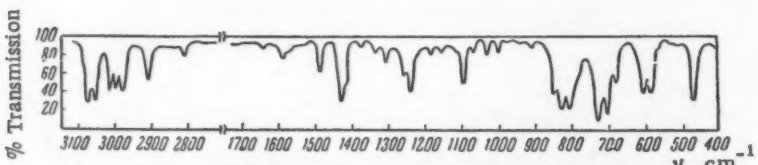


Fig. 10. The infrared spectrum of $(CH_3)_2Ge(C_6H_5)_2$.

As is apparent from Table 4, the effective electronegativities of substituents in germanium and silicon compounds differ little from one another. The exceptions are a slight increased effective electronegativity for $n\text{-}C_3H_7$ and a strongly decreased value for C_2H_5 which are apparently connected with an increase of the mutual influence of these groups and the central atom in germanium compounds. Table 5 allows one to compare the experimental values of ν_{Ge-C} with those calculated according to formula (1).

In corresponding columns of Table 5 are given: the citation of the work in which the Raman spectrum of the given substance is published (if a reference exists, otherwise the data is ours), the total electronegativity of the four substituents which are jointed to germanium in the given molecule, the calculated and experimental values of $\nu_{Ge-C'}$ and also the difference of these values $\Delta = \nu_{calc} - \nu_{exp}$. The experimental values of ν_{Ge-C} which have served as the basis of the calculation of the effective electronegativities of the radicals are marked with asterisks. The corresponding radicals are also labeled with asterisks. As can be seen in Table 5, Δ lies within the experimental limits of error in the majority of cases. The exception is $(C_3H_7)_4Ge$, the spectrum of which has two lines of equal intensity in the investigated region at 556 and 618 cm^{-1} (note that the average value 556 + 618/2 = 587 lies close to that calculated – 592).

The syntheses of the tetraalkylgermanes was realized through the organomagnesium method. The bromogermanes were obtained by the action of bromine on tetraalkylgermanes in the presence of aluminum bromide. We found that as in the case of the tetraalkylsilanes [13], tetraethylgermane on long heating with aluminum chloride gives triethylchlorogermane in yields of up to 58%. This new reaction of the organogermanium compounds can be represented by the scheme:

$$R_3GeR + AlCl_3 \longrightarrow R_3Ge\overset{R\cdots}{\underset{\cdots Cl}{}}AlCl_2 \longrightarrow R_3GeCl + RAlCl_2$$

EXPERIMENTAL

Methyltriethylgermane ($CH_3Ge(C_2H_5)_3$ (I). This was obtained in 54% yield (37.5 g) from 96 g of CH_3GeCl_3 and C_2H_5MgBr (from 36 g of Mg and 230 g of C_2H_5Br) in ether. After decomposition with water, the ether layer was dried over sodium sulfate, and the ether was removed; (I) was fractionally distilled.

TABLE 3. Sekeltal Frequencies of the Methylethylgermanes

T_d	C_{3v}	C_{2v}	C_{3v}	T_d
$(CH_3)_4Ge$	$(CH_3)_3Ge(C_2H_5)$	$(CH_3)_2Ge(C_2H_5)_2$	$CH_3Ge(C_2H_5)_3$	$Ge(C_2H_5)_4$
A_1 558 →	A_1 552 →	A_1 544 ←	A_1 536 ←	A_1 532
		B_1 574 ←	E 573 ←	F_2 572
	A_1 587 →	A_1 588 ←	A_1 592 ←	
F_2 595 →	E 600 →	B_2 600		

TABLE 4. The Effective Electronegativities of the Radicals

Radical	For germanium compounds	For silicon compounds [12]
$-Cl$	3.0	3.0
$-Br$	2.85	2.85
$-C_6H_5$	2.55	2.58
$-n\text{-}C_3H_7$	2.4	~2.0
$-CH_3$	2.0	2.0
$-CH=CH_2$	1.85	1.93
$-C_2H_5$	1.0	1.67

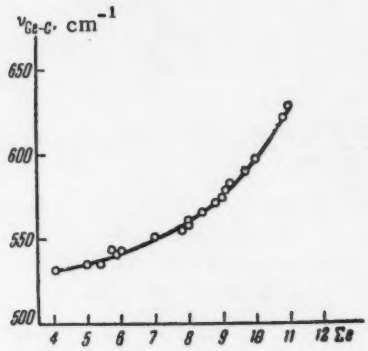


Fig. 11. The dependence of ν_{Ge-C} on Eff. EN.

Dimethyldiethylgermane $(CH_3)_2Ge(C_2H_5)_2$ (II). This was obtained in 62% yield (39.7 g) from 131 g of $(CH_3)_2GeBr_2$ and C_2H_5MgBr (from 24 g of Mg and 150 g of C_2H_5Br) under the same conditions as in the preceding experiment.

Dimethyldipropylgermane $(CH_3)_2Ge(C_3H_7)_2$ (III). This was obtained in 73% yield (30 g) from 57 g of $(CH_3)_2GeCl_2$ and C_3H_7MgBr (from 16 g of Mg and 120 of C_3H_7Br) under the conditions of the first experiment.

Dimethyldiphenylgermane $(CH_3)_2Ge(C_6H_5)_2$ (IV). This was obtained (13 g) from 87 g of $(CH_3)_2GeBr_2$ and C_6H_5MgBr (from 16 g of Mg and 150 g of C_6H_5Br) under the conditions of the first experiment.

Methyltripropylgermane $CH_3Ge(C_3H_7)_3$ (V). This was obtained in 60% yield (34 g) from 96.5 g of CH_3GeCl_3 and C_3H_7MgBr (from 36 g of Mg and 200 g of C_3H_7Br) under the conditions of the first experiment.

Triethylpropylgermane $(C_2H_5)_3GeC_3H_7$ (VI). This was obtained in 64% yield (16.5 g) from 30 g from $(C_2H_5)_3GeBr$ and C_3H_7MgCl (from 3 g of Mg and 25 g of C_3H_7Cl) under the conditions of the first experiment.

Triethylpropylgermane $(CH_3)_3GeC_3H_7$ (VII). This was obtained in 56% yield (8.5 g) from 29 g of $(CH_3)_3GeBr$ and C_3H_7MgCl (from 3.6 g of Mg and 40 g of C_3H_7Cl) under the conditions of the first experiment.

Tetrapropylgermane $(C_3H_7)_4Ge$ (VIII). This was obtained in 26% yield (61 g) from 310 g of $GeCl_4$ and 615 g of C_3H_7MgBr under the conditions of the first experiment.

TABLE 5. The Experimental and Calculated Values of ν_{Ge-C}

Compound	Reference	Σe_l	ν_{calc}	$\nu_{exp.}$	Δ
$(CH_3)_4Ge$	[5—6]	8	563	558	+5
$(CH_3)_3GeCl$	[8]	9	579	576	+3
$(CH_3)_2GeCl_2$	[8]	10	601	598	+3
CH_3GeCl_3	[8]	11	630	630	0
$(C_2H_5)_4Ge$		4	532	532	0
$(C_2H_5)_3GeCl$		6	542	544	−2
$(C_2H_5)_2GeCl_2$	[7]	8	563	561	+2
$Cl_3GeC_2H_5^*$	[7,8]	10	601	598*	+3
$(CH_3)_3Ge(C_2H_5)$		7	551	552	−1
$(CH_3)_2Ge(C_2H_5)_2$		6	542	544	−2
$CH_3Ge(C_2H_5)_3$		5	536	536	0
CH_3GeBr_3	[8]	10,55	616	617	−1
$(CH_3)_2GeBr_2$	[8]	9,7	594	592	+2
$(C_2H_5)_3GeBr$		5,85	541	543	−2
$(CH_3)_3Ge—CH=CH_2$		7,85	561	556	+5
$Cl_3Ge—CH=CH_2^*$		10,85	625	623*	+2
$(C_2H_5)_2Ge(CH=CH_2)_2$		5,7	540	545	−5
$(CH_3)_2Ge(C_6H_5)_2^*$		9,05	580	580*	0
$(CH_3)_3GeC_3H_7^*$		8,4	569	567*	+2
$(CH_3)_2Ge(C_3H_7)_2$		8,8	576	572	+4
$CH_3Ge(C_3H_7)_3$		9,2	583	584	−1
$(C_3H_7)_4Ge$		9,6	592	556,618	
$(C_2H_5)_3Ge—C_3H_7$		5,4	538	536	+2

Trimethylethylgermane $(CH_3)_3GeC_2H_5$ (IX). This was obtained in 50% yield (14.7 g) from 42 g of $C_2H_5GeCl_3$, 7.2 g of Mg and 75 g of CH_3Br under the conditions of the first experiment.

The interaction of $(C_2H_5)_4Ge$ with aluminum chloride. A mixture of 19 g of aluminum chloride and 28 g of $(C_2H_5)_4Ge$ was heated to boiling for 15 hr. During this time the boiling temperature rose from 163 to 180°. After vacuum distillation with a column there was obtained 8 g (27%) of $(C_2H_5)_3GeCl$, b. p. 170-171° (770.5 mm); d^{20}_4 1.1656, $n^{20}D$ 1.4583; found MR 45.73; calculated MR 45.85.

Three such experiments were carried out. The yield of $(C_2H_5)_3GeCl$ in these experiments was 27-58%. An equimolar mixture of $(C_2H_5)_4Ge$ and $GeCl_4$ was taken in one of these experiments. The yield of $(C_2H_5)_3GeCl$ in this experiment was 28.0% of the theoretical.

The bromination of tetraalkylgermanes in the presence of aluminum bromide. According to methods described in [13], $(C_2H_5)_3GeBr$ was obtained from 40 g of $(C_2H_5)_4Ge$, 1.5 g of $AlBr_3$, and 30 g of Br_2 at 70°. $(CH_3)_3GeBr$ was obtained in 66% yield from $(CH_3)_4Ge$ in the same way. The properties of these compounds are given in Table 6.

SUMMARY

1. The "barrier" character of the germanium atom in the vibration spectra of organogermanium molecules was established. The characteristic frequencies for the groups CH_3, C_2H_5, and n-C_3H_7 joined to Ge were found.

2. A dependence between the frequency of the fully symmetric valence vibrations of the Ge-C bond and the effective electronegativity of the substituents on the germanium atom was established. A formula is given which expresses this dependence.

3. It was found that $(C_2H_5)_4Ge$ analogously to $(C_2H_5)_4Si$, can react with aluminum chloride at 160-180°.

TABLE 6. The Properties of the Tetraalkylgermanes

Compound	% yield	B.p. °C	Pressure, mm Hg	d_4^{20}	n_D^{20}	MR		C, %		H, %	Ger, %
						found	calc				
$(C_2H_5)_2Ge(CH_3)_2$	50	107	(737,5)	0,9852	1,4215	41,43	41,74	found	44,86 44,96	10,04 9,86	45,35 45,06
								calculated	44,75	10,02	45,15
$(C_3H_7)_2Ge(CH_3)_2$	73	149,5	(746,5)	0,9660	1,4322	50,72	51,00	found	50,66 50,93	10,57 10,78	38,24 38,10
								calculated	50,83	10,72	38,44
$(C_6H_5)_2Ge(CH_3)_2$	53	145	(10)	1,180	1,5730	71,73	71,70				
$(C_2H_5)_3Ge(CH_3)$	54	135,5	(747,3)	0,9912	1,4328	45,82	46,37	found	48,15 48,12	10,50 10,54	41,73 41,57
								calculated	48,72	10,38	41,51
$(C_3H_7)_3GeCH_3$	60	189—190	(745,1)	0,9646	1,4435	59,67	60,26	found	55,26 55,30	11,32 11,30	33,34
								calculated	55,37	11,15	33,43
$(C_2H_5)_3GeC_3H_7$	64	179	(754,3)	0,9197	1,4450	55,11	55,63				
$(CH_3)_3GeC_3H_7$	56	102	(753)	0,9662	1,4158	41,74	41,74				
$(C_3H_7)_4Ge$	26	222	(745)	0,9690	1,4537	68,43	69,52				
$(CH_3)_2Ge(C_6H_5)$	50	77	(764)	0,9815	1,4085	36,92	37,11				

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

THE INFLUENCE OF THE DIMERIZATION OF FREE RADICAL INTERMEDIATES ON THE POLAROGRAPHIC WAVES OF AROMATIC ALDEHYDES AND KETONES IN AN ACID MEDIUM

S. G. Mairanovskii

The N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR
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The first stage in the process of reduction of aromatic aldehydes and ketones at the dropping mercury electrode in an acid medium is apparently [1-5] the reversible addition of an electron and a proton with the formation of free radicals

$$RR'C{=}O + e^- + H^+ \overset{el}{\rightleftarrows} RR'\dot{C}OH, \qquad (I)$$

where R = aryl, R' = H or alkyl (aryl).

The radicals either dimerize to form the corresponding pinacols

$$2RR'\dot{C}OH \xrightarrow{k_D} \underset{OH\ OH}{RR'C{-}CRR'}, \qquad (II)$$

or, if they attain a sufficiently negative potential at the electrode, they may be reduced further – to the alcohols [1-5]

$$RR'\dot{C}OH + e^- + H^+ \xrightarrow{k_{el}} RR'CHOH, \qquad (III)$$

which explains the appearance of a second wave on the polarogram.

The dimerization of the radicals which proceeds after the first and parallel with the second electrochemical reaction must influence the form and properties of both of the polarographic steps, making them differ from the ordinary diffusion waves. In the present communication the experimental peculiarities of the first wave are compared with the conclusions of the theory of reversible waves and with the dimerization of the electrode product according to Koutesky and Hanus [6]; equations are developed for the form of the second polarographic wave and the dependence of its E on the concentration of the depolarizer; these equations are compared with the experimental data. The subjects of the experiments were the polarographic reduction waves of benzaldehyde and acetophenone.

The equations of the waves and the relation for $E_{\frac{1}{2}}$. On the basis of the data of Koutesky and Hanus [6], one can show that the form of the reversible polarographic waves with rapid dimerization of the electrode product – in our case of the first wave this includes processes (I) and (II) – may be described by the equation

$$E = \varepsilon_0 - \frac{RT}{nF} \ln \frac{i^{2/3}}{\lim - i}, \qquad (1)$$

where ϵ_0 is the characteristic potential, not dependent on the concentration of the depolarizer, which corresponds to the point on the wave at which $i^{2/3} = i_{lim} - i$; $\underline{n}$ is the number of electrons participating in the electrode process (in our case n = 1); i_{lim} and $\underline{i}$ are the limiting current and the current at the given point of the wave respectively.

The relation

$$E_{1/2} = E_0 + \frac{RT}{3nF} \ln\left(\frac{k_D c_0 t}{4}\right), \tag{2}$$

was obtained [7] on the basis of an exact solution of the depolarization problem [6] for the half-wave potential $E_{\frac{1}{2}}$ of such waves, where E_0 is the redox potential of the system (I), k_D is the rate constant for the dimerization of the electrode product, c_0 is the concentration of the original compound in the bulk of the solution, t is the dropping period of the electrode.

Let us now examine the processes which determine the character of the second wave in polarograms of aldehydes and ketones. For potentials at which the second wave appears, a part of the free radicals which are formed in the first stage of the process (I), dimerize according to (II), part is reduced further according to (III), the yield of pinacol or alcohol depending on the relative rates of the processes (II) and (III). The rate of the process (III) depends on the potential of the electrode, the current of the second wave i' corresponds to the part of the free radicals which are reduced to alcohol, $i'_{lim} - i'$ = the part of the radical which separate from the electrode through dimerization and which forms the pinacol (the index' here and later designates the values related to the second wave).

If the concentration of the free radicals at the surface of the electrode is designated by c_S and one keeps in mind that the limiting currents of the first and second waves are identical, then for the conditions of the second wave on the basis of the approximate method of calculation of Brdicka-Wiesner [8, 9] or one can write

$$i'_{np} - i' = sFDc_s/\mu = sF(k_D D)^{1/2} c_s^{3/2}, \tag{3}$$

since the thickness of the reacting layer μ in which the dimerization of the radicals are occurring is equal in this case [6] to: $\mu = (D/c_s k_D)^{1/2}$. In these equations: s is the average area of the electrode; d is the coefficient of diffusion of the radicals (taken to be equal to D of the original aldehyde or ketone). For a current i' and an irreversible transfer of electrons to the radical we can write on the basis of the theory of delayed discharge of Frumkin [10]

$$i' = sFc_s k^0_{el} e^{-\alpha EF/RT}, \tag{4}$$

where k^0_{el} is the rate constant for the transfer of an electron at E = 0; α is the coefficient of transfer.

Substituting the value of c_S from (4) into (3) and taking logarithms we find the equation which describes the form of the second wave

$$E = \varepsilon'_0 - \frac{2}{3}\frac{RT}{\alpha F} \ln \frac{(i')^{3/2}}{i'_{lim} - i'}, \tag{5}$$

where the characteristic potential not dependent on the concentration is

$$\varepsilon_0' = -\frac{2}{3}\frac{RT}{\alpha F} \ln\left(\frac{k_D D}{sF}\right)^{1/2} \frac{10^{-3}}{(k^0_{el})^{3/2}}, \tag{6}$$

if the current is expressed in μA. For the potential of the half-wave we find

$$E'_{1/2} = \varepsilon'_0 - \frac{1}{3}\frac{RT}{\alpha F} \ln \frac{i'_{lim}}{2} = \varepsilon'_0 - \frac{1}{3}\frac{RT}{\alpha F} \ln \frac{1}{2} \varkappa c_0, \tag{7}$$

where $\varkappa$ is the constant of proportionality between i'_{lim} and c_0 according to the equation of Ilkovic (n = 1) in $\mu A \cdot mM^{-1}$.

It follows from (7) that as the concentration of the depolarizer in the solution increases $E_{\frac{1}{2}}$ of the second wave becomes more negative. This is connected with the fact that an increase of c_0 causes the rate of the bimolecular process (II) to increase faster than the rate of (III); therefore, in order to equalize the rates of the processes (II) and (III), which become equal to $E = E_{\frac{1}{2}}$, it is necessary to increase the rate of the electrode process, i.e., to make the potential more cathodic.

EXPERIMENTAL

The polarograms were taken according to methods described earlier with potentiometric control of the potential [11] in a thermostated cell [12] at 25°. The dropping electrode, with a scraper for the forced separation of the drop, had the characteristics: m = 1.02 mg/sec, t = 0.23 sec. The supporting electrolyte was an acetate buffer with a pH of 4.65 which contained 0.1 N CH_3COOK and 0.1 N CH_3COOH for the investigation of benzaldehyde, and for the investigation of acetophenone: 0.4 N CH_3COOK, approximately 0.4 N CH_3COOH, and 0.1 N KCl, and also about 1.5% ethyl alcohol. The increased ionic strength of the solution in the study of the waves of acetophenone promoted a clearer separation of the second wave from the background current. The first and second waves were often superimposed on one another giving a single total wave; in these cases the limiting current for the first wave in the calculations was taken to be equal to 1/2 the total height of the wave, and the magnitude of $E_{\frac{1}{2}}$ of both waves were taken to be $E_{1/4}$ and $E_{3/4}$ of the total wave.

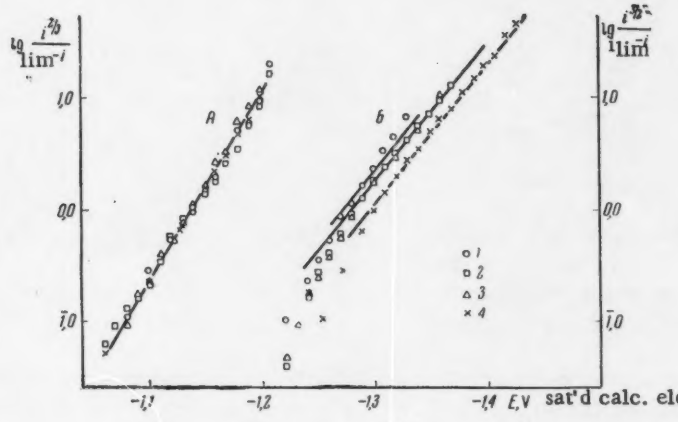

Fig. 1. The dependence of $\log \lg \frac{i^{2/3}}{i_{\overline{\lim} i}} - E$ for the first (A) and $\lg \frac{(i')^{3/2}}{i'_{\overline{\lim} i'}} - E'$ for the second (B) waves on polarograms of benzaldehyde for various concentrations of the latter: 1) 6.9; 2) 19; 3) 56; 4) $174 \cdot 10^{-5}$ M/liter. The electrolyte was an acetate buffer of pH 4.65.

The dependence of the current function $\log i^{2/3}/(i_{lim}-i)$ on the potential [according to equation (1)] is given in the left side of Fig. 1 for the first waves obtained in solutions with various concentrations of benzaldehyde. As is clear from Fig. 1, the experimental points fall rather well on a straight line which has the theoretically predicted slope of approximately 60 mv [see equation (1)]. The half-wave potential $E_{\frac{1}{2}}$ of the first wave becomes more positive with an increased concentration of benzaldehyde (see line 1 on Fig. 2), the slope of the graph $\Delta E/\Delta \log c_0 \approx$ 20 mv coinciding with the magnitude predicted by equation (2): 19.7 mv. These data indicate that the first wave of the polarogram of benzaldehyde actually has a reversible electrochemical stage. The value ϵ_0, as is apparent from Fig. 1, is equal to 1.140 v (relative to the saturated calomel electrode).

The dependence of the current function $\log (i')^{3/2}/(i'_{lim}-i')$ on E according to equation (5) is given on the right side of Fig. 1 for the second wave of benzaldehyde. The experimental values obtained with different concentrations of depolarizer are crowded rather closely together. The upper part of the graphs is linear as is required by equations (5); the lower part is distorted because of the proximity of the first wave. The fact is that the values of i' are found by subtraction of the limiting current i'_{lim} from the total observed current. Since the first and second wave occur on the potential axis directly after one other (see Fig. 3), in order to obtain the true value of i' one should subtract from the observed current not the magnitude i'_{lim}, which at the potentials at the beginning of the

second may not yet be attained, but the true value of the current of the first wave i at the given potential; this can be calculated from the equation of the first wave (1).

The dependence of $E'_{\frac{1}{2}}$ of the second wave on the concentration of benzaldehyde is given in the upper part of Fig. 2. As concentration of benzaldehyde increases $E'_{\frac{1}{2}}$ of the second wave in agreement with the theory becomes more negative, and this together with the movement of $E_{\frac{1}{2}}$ of the first wave toward anodic potentials leads to a separation of the waves on the polarogram of benzaldehyde (see Fig. 3). For the second wave the value of $\Delta E'_{\frac{1}{2}}/\Delta \log c_0 \approx -44$ mv.

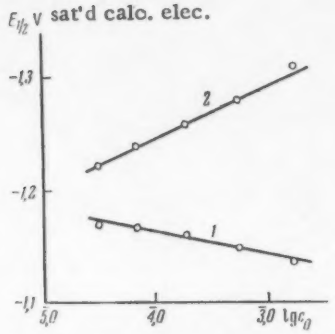

Fig. 2. The dependence of $E_{\frac{1}{2}}$ of the first (1) and second (2) waves of benzaldehyde on its concentration in the solution.

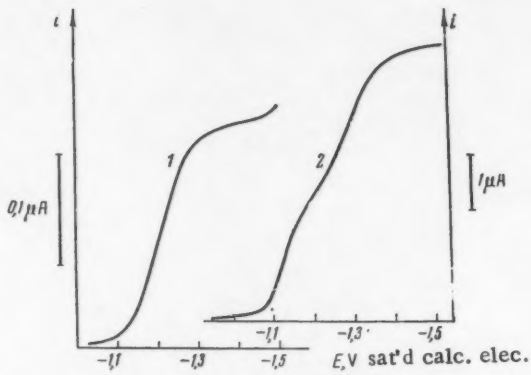

Fig. 3. Polarograms of benzaldehyde for $c_0 = 6.9 \cdot 10^{-5}$ M (1) and $1.74 \cdot 10^{-3}$ M (2).

A comparison of expressions (5) and (7) shows that $\Delta E'_{\frac{1}{2}}/\Delta \log c_0$ must be equal to half the reciprocal value of the slope of the graph of $\log (i')^{3/2}(i_{lim} - i') - E$. As is apparent from the right side of Fig. 1, the reciprocal value of the slope of the logarithmic graph is equal to approximately 82 mv, i.e., the theoretical relation indicated above is approximately observed.

From the slope of the logarithmic graph Fig. 1-B according to (5), the transfer coefficient was determined for the second wave of benzaldehyde, $\alpha = 0.48$. The value ϵ'_0 in the concentration interval studied ranged from -1.278 to -1.296 v.

Similar results were also obtained for the wave of acetophenone. Its first wave was satisfactorily described by equation (1) with $\epsilon_0 = -1.300$ v (referred to the saturated calomel electrode) $\Delta E_{\frac{1}{2}}/\Delta \log c_0$ of the first wave was close to 20 mv. $E'_{\frac{1}{2}}$ of the second wave of acetophenone becomes more negative as its concentration increases; the value of $\Delta E'_{\frac{1}{2}}/\Delta \log c_0$ could not be established with sufficient sensitivity for the second wave, since the second wave was very poorly defined at low concentrations of acetophenone. The reciprocal value of the slope of the logarithmic graph of the second wave at $c_0 \geq 1$ mM was equal to 88 mv, $\alpha = 0.45$, $\epsilon'_0 = -1.510$ v.

After the present article had been sent to the publisher the author became aware of the work of Suziki and Elving [13] in which it was impossible to obtain a clear picture of the influence of the dimerization of the radicals from the polarographic waves of the reduction of benzophenone.

On the basis of a comparison of the data of the present and cited work, it is possible to conclude that the influence of the kinetics of dimerization on the waves must appear more clearly in the absence of the formation of slightly soluble products at the electrode surface which inhibit the electrode process, i.e., for a very short period electrodes and comparatively small concentrations of low molecular aldehydes and ketones. From this point of view one may easily also explain the movement of the straight line B of Fig. 1 toward negative potentials as c_0 is increased this movement is obviously conditioned by some inhibition of the electrode process of the second wave by the products which have accumulated at the electrode.

SUMMARY

1. The form of the first wave in the polarograms of benzaldehyde and acetophenone is described by an equation for a reversible wave with subsequent rapid bimolecular interaction of the reduced products; and its half-wave

potential becomes more positive with an increase of the concentration of the depolarizer, thus confirming the reversible character of the electrochemical reaction and the fact that it is followed by a rapid dimerization of the electrode product.

2. Equations are derived for the form of the second wave in the polarograms of aromatic aldehydes and ketones and for the dependence of its half-wave potential on the concentration of the depolarizer; these I found to be in agreement with the experimental data.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

ORGANIC AND BIOLOGICAL CHEMISTRY

ACYL AND ALKOXY DERIVATIVES OF DICYCLOPENTADIENYLTITANIUM AND THE REFRACTION INCREMENT OF THE π-C_5H_5Ti GROUP

A. N. Nesmeyanov, O. V. Nogina, A. M. Berlin, A. S. Girshovich, and G. V. Shatalov

Institute of Heteroorganic Compounds, Academy of Sciences, USSR
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Dicyclopentadienyltitanium derivatives containing acyl groups have not been described in the literature.* By the action of acetate and methacrylate salts on dicyclopentadienyltitanium dichloride we obtained acyl derivatives:

$$(C_5H_5)_2TiCl_2+2CH_3COOK \rightarrow (C_5H_5)_2Ti(OCOCH_3)_2+2KCl$$

$$(C_5H_5)_2TiCl_2+2CH_2=\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-COOK \rightarrow (C_5H_5)_2Ti(OCO\overset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}=CH_2)_2+2KCl$$

$$(C_5H_5)_2Ti\begin{matrix}OC_2H_5\\Cl\end{matrix}+CH_2=\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-COOK \longrightarrow (C_5H_5)_2Ti\begin{matrix}OC_2H_5\\OCOC(CH_3)=CH_2\end{matrix}+KCl$$

G. S. Kolesnikov, S. L. Davydova, N. V. Klimentova, and G. V. Shatalov showed that dicyclopentadienylethoxytitanium methacrylate and dicyclopentadienyltitanium dimethacrylate are able to polymerize and to copolymerize with styrene and with methyl methacrylate.

We carried out the hydrolysis of dicyclopentadienyltitanium diacetate. It was found that, in addition to the formation of titanoxane links, there was complete elimination of one cyclopentadienyl ring from the titanium atom:

$$2\,(C_5H_5)_2Ti(OCOCH_3)_2+H_2O \longrightarrow [C_5H_5Ti(OCOCH_3)_2]_2O+2C_5H_6$$

It should be noted that we observed the elimination of one ring also in the course of the boiling of an alcoholic solution of dicyclopentadienyltitanium dichloride, but in this case the elimination reaction occurred only to a slight extent:

$$(C_5H_5)_2TiCl_2+C_2H_5OH \longrightarrow C_5H_5TiCl_2(OC_2H_5)+C_5H_6$$

The elimination of two cyclopentadienyl rings from dicyclopentadienyltitanium dichloride occurs [2] in the cohydrolysis of a dialkyldichlorosilane with dicyclopentadienyltitanium dichloride in alkaline and acid media.

Until now, only one alkoxy derivative of dicyclopentadienyltitanium was known. We obtained dicyclopentadienylethoxytitanium chloride $(C_2H_5)_2Ti(OC_2H_5)Cl$ by the action of cyclopentadienylsodium on ethoxytitanium trichloride [3].

There has appeared a description of an unsuccessful attempt [4] to prepare dicyclopentadienylmethoxytitanium chloride by the action of cyclopentadienylsodium on cyclopentadienylmethoxytitanium dichloride $C_5H_5Ti(OCH_3)Cl_2$. Alkoxy derivatives of monocyclopentadienyltitanium are described in [3, 4]. It was found that alkoxydicyclopentadienyltitanium and (aryloxy)dicyclopentadienyltitanium chlorides may be readily prepared by the action of alcohols and of phenols on $(C_5H_5)_2TiCl_2$ in presence of a tertiary amine

* After this paper had been sent to press there appeared a paper by Razuvaev, Latyaeva, and Vyshinskaya [1] which described the preparation of dicyclopentadienyltitanium diacetate and dibenzoate.

$$(C_5H_5)_2TiCl_2+ROH+(C_2H_5)_3N \longrightarrow (C_5H_5)_2TiCl(OR)+(C_2H_5)_3N\cdot HCl,$$

in which R = C_2H_5; $CH_2=CH-CH_2$; C_6H_5.

Monoalkoxy- and mono(aryloxy)-dicyclopentadienyltitanium compounds are orange-yellow crystalline substances, very sensitive to the action of atmospheric moisture and of low thermal stability. Thus, in absence of moisture at room temperature (allyloxy)dicyclopentadienyltitanium chloride turns red after one day and is converted into a very viscous mass; at 0° it remains unchanged for a month.

In the Macromolecular Compounds Laboratory of the Institute of Heteroorganic Compounds, V. V. Korshak, A. M. Sladkov, L. K. Luneva, and A. S. Girshovich have prepared a polymer of (allyloxy)dicyclopentadienyltitanium chloride and its copolymers with styrene and methyl methacrylate.

In this paper we describe also dicyclopentadienyl(trimethylsiloxy)titanium chloride $(C_5H_5)_2Ti\langle^{Cl}_{OSi(CH_3)_3}$, which was prepared by the action of cyclopentadienylsodium on (trimethylsiloxy)titanium trichloride. The course of the reaction was not the same as in the case of an alkoxytitanium trichloride [3]. From the complex mixture of products we isolated not only $(C_5H_5)_2Ti\langle^{Cl}_{OSi(CH_3)_3}$ but also $C_5H_5Ti[OSi(CH_3)_3]_3$ and $(C_5H_5)_2TiCl_2$. This result is probably due to the simultaneous occurrence of the reactions:

$$(CH_3)_3SiOTiCl_3+2C_5H_5Na \longrightarrow (C_5H_5)_2Ti\langle^{Cl}_{OSi(CH_3)_3}+2NaCl$$

$$(CH_3)_3SiOTiCl_3+C_5H_5Na \longrightarrow C_5H_5TiCl_3+(CH_3)_3SiONa$$

$$C_5H_5TiCl_3+C_5H_5Na \longrightarrow (C_5H_5)_2TiCl_2+NaCl$$

$$C_5H_5TiCl_3+3(CH_3)_3SiONa \longrightarrow C_5H_5Ti[OSi(CH_3)_3]_3+3NaCl$$

TABLE

Substance	n_D^{20}	d_4^{20}	Mol. wt.	MR found	Sum of atomic refractions of C, H, and O	Increment of π-C_5H_5Ti	Homologs difference	
							found	calc.
$(C_2H_5O)_3TiC_5H_5$	1,5500	1,1103	248,170	71,204	35,937	35,27	—	—
$(n\text{-}C_3H_7O)_3TiC_5H_5$	1,5282*	1,0509*	290,248	85,072	49,791	35,28	4,62	4,62
$(n\text{-}C_4H_9O)_3TiC_5H_5$**	1,5224	1,0250	332,326	98,950	63,645	35,30	4,63	4,62

* These results were obtained at 23.5°; $n^{20}D$ 1.5310.

** $C_5H_5Ti(OC_4H_9\text{-}n)_3$ is here described for the first time.

We determined the refraction increment of the group formed by titanium and the cyclopentadienyl ring (including the atomic refraction of the titanium) by the application of our previous results on trialkoxy-π-cyclopentadienyltitaniums [3]. The results are given in the table. According to our results the increment of the π-C_5H_5Ti group, including the atomic refraction of titanium, is 35.28.

EXPERIMENTAL*

Preparation of dicyclopentadienyltitanium diacetate. To a solution of 4 g (0.016 mole) of $(C_5H_5)_2TiCl_2$ in 150 ml of chloroform we added 4.75 g (0.048 mole) of potassium acetate; the mixture was refluxed for three hours. We then added a further 4 g (0.041 mole) of potassium acetate, the reaction mixture was boiled for three hours, and the precipitate formed was filtered off; from the filtrate solvent was distilled off at a residual pressure of 15-20 mm.

* All experiments were carried out with completely dry starting substances and solvents under conditions that precluded access of atmospheric moisture.

The weight of the crystalline mass that remained was 4.38 g (93%). The substance consisted of dark-orange crystals, readily soluble in chloroform and tetrahydrofuran, less soluble in benzene, and quite insoluble in petroleum ether not stable to heating; m. p. 126-128° (from benzene). Found: C 56.64, 56.83; H 5.63, 5.80; Ti 16.28, 16.07%; mol. wt. 288; 299. $(C_5H_5)_2Ti(OCOCH_3)_2$. Calculated: C 56.77; H 5.41; Ti 16.17%; mol. wt. 296.

Hydrolysis of dicyclopentadienyltitanium diacetate. To a solution of 3 g (0.01 mole) of $(C_5H_5)_2Ti(OCOCH_3)_2$ in 60 ml of tetrahydrofuran we added 0.0912 g (0.005 mole) of water in 10 ml of tetrahydrofuran. The reaction mixture was refluxed for one hour. Solvent was driven off at a residual pressure of 15-20 mm and collected in a trap (−60°); to this we added thallium reagent (4.05 g of Tl_2SO_4, 1.62 g of KOH in 32.4 ml of water) [5]. The precipitate formed was filtered off, washed with cold, water, dried, and sublimed at a residual pressure of 2 mm from a bath heated to 110-114°; weight 2.64 g (96.7%). Found: C 22.32, 22.26; H 1.94, 1.93; Tl 75.79, 75.68%. C_5H_5Tl. Calculated: C 22.29; H 1.87; Tl 75.84%.

The residue remaining after the removal of solvent was soluble in chloroform and tetrahydrofuran, difficultly soluble in benzene, dioxane, and cyclohexane, and quite insoluble in petroleum ether; we did not succeed in recrystallizing it. Found: C 46.46, 46.41; H 4.85, 4.73; Ti 20.55, 20.30%; mol. wt. 473; 472 (cryoscopic method in bromoform). $[C_5H_5Ti(OCOCH_3)_2]_2O$. Calculated: C 45.21; H 4.63; Ti 20.03%; mol. wt. 478.

Reaction of dicyclopentadienyltitanium dichloride with ethanol. A solution of 6 g of $(C_5H_5)_2TiCl_2$ in 350 ml of ethanol was refluxed in a stream of nitrogen for eight hours. The reaction mixture was cooled. Precipitated unchanged $(C_5H_5)_2TiCl_2$ was filtered off. The solution was vacuum-evaporated (15-20 mm) down to 100 ml. Precipitated $(C_5H_5)_2TiCl_2$ was again filtered off. The residue was evaporated to dryness and extracted with petroleum ether (30-50°); the extract was evaporated, and the residue was recrystallized from petroleum ether. The product consisted of light-yellow needles. Found: C 35.99, 36.21; H 4.17, 4.27; Ti 21.22, 21.73; Cl 30.55, 31.22%. $C_5H_5Ti(OC_2H_5)Cl_2$. Calculated: C 36.71; H 4.40; Ti 20.92; Cl 30.97%.

In an analogous experiment alcohol was distilled of at a residual pressure of 15-20 mm into a cooled (−60°) receiver; we added thallium reagent, as described above. The precipitate formed was filtered off, washed with cold water, dried in a desiccator over $CaCl_2$, and sublimed at 2 mm from a bath at 110-114°. Found: C 22.19, 22.22; H 1.82, 1.88; Tl 75.96, 75.65%. Calculated: C 22.29; H 1.87; Tl 75.84%.

Preparation of dicyclopentadienylethoxytitanium methacrylate. With vigorous stirring, 8.79 g (0.07 mole) of potassium methacrylate was added to a solution of 8.79 g (0.07 mole) of potassium methacrylate was added to a solution of 9.95 g (0.030 mole) of dicyclopentadienylethoxytitanium chloride in 375 ml of chloroform. The reaction mixture was heated for five hours in a bath at 60-70°. The precipitated potassium chloride and excess of potassium methacrylate were filtered off. Chloroform was vacuum-distilled off at 15-20 mm in a bath at 30-40°. The yield of dicyclopentadienylethoxytitanium methacrylate was quantitative. The product was recrystallized from a 1:1 mixture of benzene and petroleum ether; m. p. 165-166° in a sealed capillary. Found: C 62.40, 62.36; H 6.29, 6.24; Ti 14.13, 14.23%; mol. wt. 310.3 (cryoscopic method in benzene). $C_5H_5)_2Ti(OC_2H_5)$ $(O_2C_4H_5)$. Calculated C: 62.37; H 6.49; Ti 15.54%; mol. wt. 308.1.

The dicyclopentadienylethoxytitanium methacrylate so obtained was readily soluble in benzene, acetone, and chloroform, but insoluble in petroleum ether.

Synthesis of dicyclopentadienyltitanium dimethacrylate. To a solution of 2.37 g (0.009 mole) of dicyclopentadienyltitanium dichloride in 200 ml of chloroform we added 2.63 g (0.021 mole) of potassium methacrylate. The reaction mixture was vigorously stirred and heated for three hours in a bath at 60-70°. Precipitated potassium chloride was filtered off. To the filtrate we again added potassium methacrylate (1.96 g; 0.057 mole), and the mixture was stirred further under the same conditions for two hours. Precipitated potassium chloride and excess of potassium methacrylate were filtered off. Chloroform was vacuum-distilled off at 15-20 mm in a bath at 30-40°. Yield 2.98 g (90%). The product was precipitated from benzene solution with petroleum ether. The resulting dicyclopentadienyltitanium dimethacrylate was dried, first on the filter in a stream of dry air, and then in a vacuum at 1-2 mm in a bath at 60-70° for 90 minutes. In a sealed capillary the product melted over a wide range of temperature, 135-150°. Found: C 62.37, 62.18; H 6.13, 5.99; Ti 13.98, 13.70%; mol. wt. 347.1 (cryoscopic method in benzene). $(C_5H_5)_2Ti(O_2C_4H_5)_2$. Calculated: C 62.08; H 5.79; Ti 13.75%; mol. wt. 348.2.

The dicyclopentadienyltitanium dimethacrylate so obtained was an orange crystalline substance, soluble in benzene, difficultly soluble in chloroform, carbon tetrachloride, and methylene chloride, and insoluble in petroleum ether.

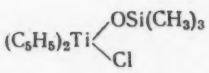
Preparation of dicyclopentadienylethoxytitanium chloride. A mixture of 1.6 g (0.035 mole) of ethanol and 1.8 g (0.0178 mole) of triethylamine was added with vigorous stirring to a solution of 4 g (0.0160 mole) of dicyclopentadienyltitanium dichloride in 400 ml of benzene in a bath at 50-60°. Stirring and heating were continued for three hours. The precipitate of triethylamine hydrochloride formed was filtered off, washed with benzene, and dried at a residual pressure of 2-3 mm in a bath at 100°; m. p. 251° (the literature [6] gives 253°). Yield 2.21 g (99%). Benzene was distilled from the filtrate at a residual pressure of 15-20 mm. We obtained 4.1 g of a bright-yellow crystalline substance. The product was recrystallized from a 1:1 mixture of benzene and petroleum ether. In a sealed capillary the substance had m. p. 88-89°. The literature [3] gives m. p. 89-91°.

Preparation of dicyclopentadienylphenoxytitanium chloride. The procedure was as in the preceding experiment. A mixture of 1.51 g (0.016 mole) of phenol in 10 ml of benzene and 1.8 g (0.0178 mole) of triethylamine was added slowly to a solution of 4 g (0.016 mole) of dicyclopentadienyltitanium dichloride in 500 ml of benzene. The reaction mixture was stirred and heated in a bath at 50-60° for 3.5 hours. The yield of triethylamine hydrochloride was 2.2 g (98.5%); m. p. 250°. The literature [6] gives m. p. 253°. From the filtrate we obtained 4.8 g of resinous substance after the removal of benzene by distillation. The product was recrystallized from petroleum ether (35-55°). The orange-yellow crystalline substance melted at 71-73° in a sealed capillary. Found: C 62.34, 62.34; H 5.13, 5.34; Ti 15.54, 15.74; Cl 10.39, 10.68%; mol. wt. 308.7 (cryoscopic method in benzene). $(C_5H_5)_2Ti(OC_6H_5)Cl$. Calculated: C 62.66; H 4.9; Ti 15.63; Cl 11.58%; mol. wt. 306.4.

Preparation of (allyloxy)dicyclopentadienyltitanium chloride. To a solution of 6 g (0.024 mole) of dicyclopentadienyltitanium dichloride in 500 ml of benzene we added 2.67 g (0.0264 mole) of triethylamine; then, with vigorous stirring and heating of the reaction mixture in a bath at 35-40°, we made dropwise addition of 1.4 g (0.0242 mole) of allyl alcohol. After two hours the precipitate of triethylamine hydrochloride was filtered off and treated as in the preceding experiment. Yield 3.05 g (92.5%); m. p. 250°. The literature [6] gives m. p. 253°. Benzene was distilled from the filtrate at 15-20 mm. We obtained 6 g of brown resinous substance. After recrystallization from petroleum ether (b. p. 35-50°) we obtained a substance in the form of orange-yellow crystals, m. p. 57-58° in a sealed capillary. Found: C 57.40, 57.27; H 5.72, 5.94; Ti 17.97, 17.52; Cl 13.99, 13.90%; mol. wt. 267.8 (cryoscopic method in benzene). $(C_5H_5)_2Ti(OC_3H_5)Cl$. Calculated: C 57.69; H 5.55; Ti 17.71; Cl 13.13%; mol. wt. 270.4.

Preparation of tributoxycyclopentadienyltitanium. A solution of cyclopentadienylsodium prepared from 1.244 g (0.054 mole) of sodium in 70 ml of tetrahydrofuran and 4.83 g (0.073 mole) of cyclopentadiene was cooled with ice and salt and added dropwise with vigorous stirring to a solution of 16.36 g (0.054 mole) of $(C_4H_9O)_3TiCl$ in 50 ml of tetrahydrofuran, also cooled with ice and salt. The reaction mixture was stirred further with cooling for three hours. The precipitated NaCl was filtered off and washed carefully with tetrahydrofuran. The residue remaining after the removal of solvent, which amounted to 14.75 g (82%), was vacuum-distilled. We obtained a slightly yellowish liquid, b. p. 124.5-125.5° (0.5-1 mm), which distilled with some decomposition. The substance was redistilled at 10^{-5} mm; $n^{20}D$ 1.5224; d^{20}_4 1.0250. Found: C 60.76, 60.65; H 9.68, 9.70; Ti 14.55, 14.63%. $C_5H_5Ti(OC_4H_9)_3$. Calculated: C 61.43; H 9.70; Ti 14.41%. Analysis of another sample: Found: C 61.22, 61.33; H 10.15, 10.13; Ti 15.23, 15.26%. $C_5H_5Ti(OC_4H_9)_3$. This was a liquid which decomposed instantaneously under the action of atmospheric moisture; soluble in all the usual organic solvents.

Reaction of $(CH_3)_3SiOTiCl_3$ with cyclopentadienylsodium. $(CH_3)_3SiOTiCl_3$ was prepared by Andrianov and Kurasheva's method [7], and it was always distilled before use in a reaction. The procedure was similar to that of the preceding experiment. A solution of cyclopentadienylsodium prepared from 3.57 g (0.155 mole) of sodium in 100 ml of tetrahydrofuran and 15 ml (0.182 mole) of cyclopentadiene was poured into a solution of 18.92 g (0.077 mole) of $(CH_3)_3SiOTiCl_3$ was warmed slightly and poured into the cooled tetrahydrofuran as a liquid. The reaction mixture was filtered from the precipitate, which was washed carefully with tetrahydrofuran and chloroform. The residue remaining after the removal of solvents amounted to 18.68 g and consisted of a complex mixture of products. By extraction with petroleum ether at room temperature we obtained 2.80 g of a bright-orange crystalline substance, m. p. 137.0-137.5° (from petroleum ether or methylene chloride) readily soluble in all the usual organic solvents and stable in the solid state. Titanium was determined by a polarographic method. Found: Ti 15.58, 15.15%; mol. wt. 297.7; 316.3.



Calculated: Ti 15.82%; mol. wt. 302.7.

From the mother liquor remaining after the separation of $(C_5H_5)_2Ti\langle^{OSi(CH_3)_3}_{Cl}$ vacuum distillation gave a colorless mobile liquid; b. p. 138-139° (4 mm); 92.5-93.5° (1 mm); $n^{20}D$ 1.4582; d^{20}_4 0.9436. Found: C 44.21, 44.03; H 8.70, 8.80; ash 68.07, 67.95%; mol. wt. 367.2. $C_5H_5Ti[OSi(CO_3)_3]_3$. Calculated: C 44.18; H 8.47; ash 68.3%; mol. wt. 380.5.

Apart from these substance we isolated also: 1) $(C_5H_5)_2TiCl_2$, m. p. 281-282° (The literature [8] gives m. p. 289 ± 2°. Found: C 48.28, 48.63; H 4.46, 4.49; Ti 19.33, 19.52; Cl 28.35, 28.25%. $(C_5H_5)_2TiCl_2$. Calculated: C 48.23; H 4.05; Ti 19.27; Cl 28.48%); and 2) an infusible amorphous powder, soluble only in N,N-dimethylformamide, of unestablished structure.

SUMMARY

1. The following dicyclopentadienyl titanium derivatives containing acyl groups were synthesized:

$(C_5H_5)_2Ti(OCOCH_3)_2$; $(C_5H_5)_2Ti\langle^{OC_2H_5}_{OCOC=CH_2}{}^{CH_3}$ and $(C_5H_5)_2Ti(OCOC(CH_3)=CH_2)_2$

2. It was shown to be possible to prepare monoalkoxy- and mono(aryloxy)-dicyclopentadienyltitanium derivatives by the action of alcohols and phenols on $(C_5H_5)_2TiCl_2$ in presence of a tertiary amine.

3. By the action of C_5H_5Na on $(CH_3)_3SiOTiCl_3$ we obtained $(C_5H_5)_2Ti\cdot[OSi(CH_3)_3]Cl$ and $C_5H_5Ti[OSi(CH_3)_3]_3$.

4. The refraction increment of the titanium-cyclopentadienyl ring group (including the atomic refraction of titanium) was determined and found to be 35.28.

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ADDITION OF NUCLEOPHILIC REAGENTS TO 2-CYANOVINYL KETONES

A. N. Nesmeyanov, M. I. Rybinskaya, and L. V. Rybin

Institute of Heteroorganic Compounds, Academy of Sciences, USSR

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The addition of nucleophilic reagents to unsaturated compounds containing an electron-accepting group conjugated with the double bond has been investigated for various reactions. One example is the fairly extensively investigated Michael condensation. It has been shown purely qualitatively [1] that the readiness with which this condensation goes and the yields of products diminish in the series

$$C{=}C{-}\underset{\displaystyle H}{\underset{|}{C}}{=}O > C{=}C{-}\underset{\displaystyle R}{\underset{|}{C}}{=}O > C{=}C{-}\underset{\displaystyle OR}{\underset{|}{C}}{=}O \geqslant C{=}C{-}C{\equiv}N > C{=}C{-}NO_2$$

which coincides with the series of diminishing electromeric effect obtained by Arndt and co-workers [2] on the basis of the investigation of the acidity and enolizability of tautomeric systems.

It is known that the addition of the nucleophilic group A occurs in the β-position to the electron-accepting residue X:

$$\underset{(+\delta)}{CH_2{=}\overset{\curvearrowright}{C}H{-}\overset{\curvearrowright}{X}} + HA \longrightarrow \underset{\displaystyle A}{\underset{|}{CH_2}}{-}CH_2X$$

Until now very little investigation has been given to the addition of nucleophilic reagents to compounds with a double bond conjugated with two electron-attracting groups. When two different electron-attracting groups are present in such a system there arises the question of the orientation of the nucleophilic addition. Nucleophilic addition has been investigated most fully for the system in 3-acylacrylic acids and esters [3-7], and it has been found that the double bond is conjugated in the main with the carbonyl group, and it is the latter that orients the addition of the nucleophilic residue in the β-position.*

$$R{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}CH{=}CHCOOR' + HA \rightarrow R\underset{\displaystyle O}{\underset{\|}{C}}{-}CH_2{-}\underset{\displaystyle A}{\underset{|}{CH}}{-}COOR'$$

$R' = H$ Alk

It has been shown that the addition of water and of hydrogen bromide to 3-(phenylsulfonyl)acrylophenone goes as follows [8]:

$$C_6H_5CO{-}CH{=}CH{-}SO_2C_6H_5 \xrightarrow{HA} C_6H_5COCH_2\underset{\displaystyle A}{\underset{|}{CH}}{-}SO_2C_6H_5,$$

A = OH, Br.

The course of the addition of water and of alcohol to 3-nitroacrylic acid is also known [9]; here NO_2 has the strongest polarizing effect on the double bond

$$\underset{\displaystyle NO_2}{\underset{|}{CH}}{=}\underset{\displaystyle COOH}{\underset{|}{CH}} + HA \rightarrow \underset{\displaystyle NO_2}{\underset{|}{CH_2}}{-}\underset{\displaystyle COOH}{\underset{|}{CH}}{-}A$$

A = OH, CH_3O.

* We shall not give a full review here of addition to 3-acrylacrylic acids.

In 4,4,4-trifluorocrotonic acid and its amide and esters the groups COOH, $CONH_2$, and $COOC_2H_5$ are stronger orientants than the CF_3 group [10, 11]

$$CF_3CH=CHCOX + HA \rightarrow CF_3-\underset{\displaystyle A}{\underset{|}{CH}}-CH_2COX$$

$$X = OH,\ OC_2H_5,\ NH_2,\ A = OH,\ NH_2,\ Br$$

It is interesting that an accumulation of CF_3 groups leads to a reversal of the direction of addition, as Knunyants and co-workers showed [12]*

$$(CF_3)_2C=CH-COOR \xrightarrow{HA} (CF_3)_2CH-\underset{\displaystyle A}{\underset{|}{CH}}-COOR$$

For $R = H,\ A = OH$

For $R = C_2H_5,\ A = NH_2,\ N = (CH_2)_5,\ NH(CH_2)_2OH$

The 2-cyanovinyl ketones that we synthesized [13] also form a system in which a carbonyl and a cyano group are conjugated with a double bond. We have already investigated the reactions of secondary aliphatic amines [14] and of benzenethiol [15] with these compounds. In the present paper we studied the addition of other nucleophilic reagents: aniline, N-methylaniline, sodium bisulfite, and 2-naphthol.

We found that aniline and N-methylaniline readily add to 2-cyanovinyl ketones in methanol solution with formation of the corresponding 3-acyl-2-anilino- and 3-acyl-2-N-methylanilino-propionitriles:

$$RCOCH=CHCN + NHR'C_6H_5 \rightarrow RCOCH_2\underset{\displaystyle R'-N-C_6H_5}{\underset{|}{CH}}-CN,$$

where $R = CH_3-,\ C_6H_5-,\ o\text{-}ClC_6H_4,\ p\text{-}BrC_6H_4;\ R' = H$

$R = C_6H_5-;\ R' = CH_3-$

The addition products were colorless well crystallizing substances. Their structures were proved for the cases of 3-acetyl-2-anilinopropionitrile and 2-anilino-3-benzoylpropionitrile by the scheme that we developed earlier [14]:

$$RCOCH_2\ \underset{\displaystyle NHC_6H_5}{\underset{|}{CHCN}} \xrightarrow{NaOH} RCOCH=CHNHC_6H_5$$

$R = CH_3-;\ C_6H_5-$

As a result we isolated and identified the already known 2-anilinovinyl methyl and 2-anilinovinyl phenol ketones [16].

The 2-anilino-3-benzoyl- and 3-benzoyl-2-N-methylanilino-propionitriles obtained were readily hydrolyzed with perchloric acid to the corresponding amides:

$$C_6H_5COCH_2\ \underset{\displaystyle R-N-C_6H_5}{\underset{|}{CHCN}} \xrightarrow{70\ \%\ HClO_4} C_6H_5COCH_2\underset{\displaystyle R-NC_6H_5}{\underset{|}{CH}}-CONH_2$$

$R = H, -CH_3$

$R = H$

$$C_6H_5COCH=CHCONH_2 + NH_2C_6H_5$$

2-Anilino-3-benzoylpropionamide was obtained also by the reaction of 3-benzoylacrylamide with aniline, which was to be expected since the $CONH_2$ group is known to be a stronger electron-accepting group than carboxyl, and the latter is weaker than the keto group in competing conjugation. We did not succeed in hydrolyzing these amides or the nitriles themselves to the corresponding acids. The process is probably very complex and with concentrated hydrochloric acid, for example, colored noncrystallizing powders are formed, and in an alkaline medium the substance is destroyed.

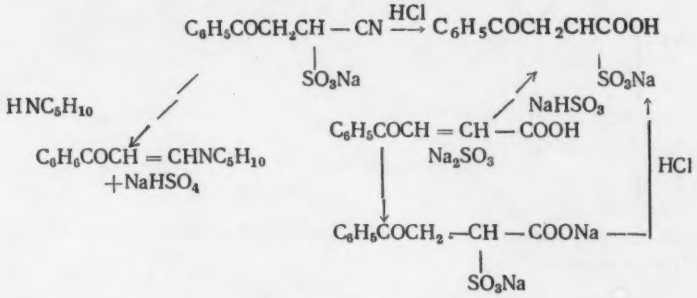
* We do not examine in greater detail cases in which there are other substituents apart from two electron-accepting groups in the α- and β- positions to the double bond.

Aryl 2-cyanovinyl ketones undergo ready addition with sodium bisulfite in an aqueous-alcoholic medium, and in presence of excess of bisulfite a second molecule adds at the carbonyl group. To avoid this, the aryl 2-cyanovinyl ketone is taken in 5% excess, and to purify the product thoroughly from the adduct with two molecules of sodium bisulfite crystallization is carried out with the addition of 1-2 drops of concentrated HCl

$$ArCOCH=CHCN + NaHSO_3 \rightarrow ArCOCH_2CH(SO_3Na)-CN$$

Ar = C_6H_5—, o-Cl — C_6H_4—, o-BrC_6H_4—, p-BrC_6H_4—.

The resulting sodium 2-aroyl-1-cyanoethanesulfonates generally contain water of crystallization, which may be removed by heating the product in a vacuum over P_2O_5. These salts are very soluble in water. When sodium 2-benzoyl-1-cyanoethanesulfonate is boiled with concentrated hydrochloric acid, the CN group is hydrolyzed to carboxyl. The resulting substance crystallizes well from concentrated hydrochloric acid

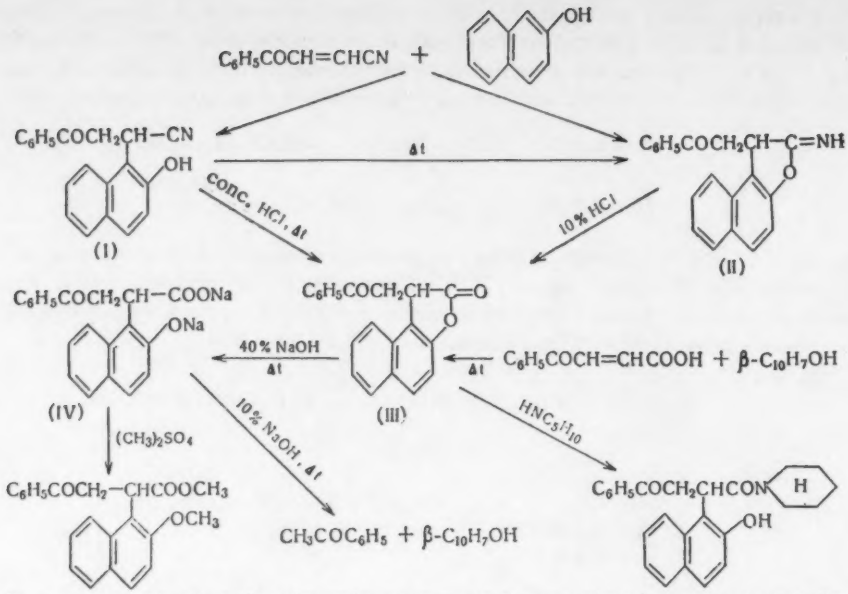


The same substance (coincides in melting point and in ultraviolet and infrared spectra) was prepared by boiling the disodium salt 2-benzoyl-1-carboxyethanesulfonic acid with concentrated hydrochloric acid (this disodium salt has been described previously [7]), which is confirmation of the structure of the adducts obtained. We found that the same salt is obtained by the reaction of 3-benzoylacrylic acid with sodium bisulfite.

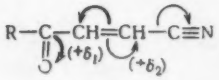
We did not succeed in eliminating a molecule of HCN from sodium 3-benzoyl-2-cyanoethanesulfonate with the aid of a base as in the case of adducts with amines. Thus, treatment with caustic alkali led to the destruction of the substance; when it was boiled with excess of triethylamine the original salt was isolated unchanged; and in the reaction with piperidine we isolated phenyl 2-piperidinovinyl ketone and sodium bisulfite.

We did not succeed in finding the conditions for the addition of phenols of the benzene series of 2-cyanovinyl ketones. However, 2-cyanovinyl phenyl ketone readily reacts with 2-naphthol in presence of catalytic amounts of calcium hydroxide. When the reaction is carried out in a 10:1 water-dioxane mixture in the cold in presence of calcium hydroxide, we obtain 3-benzoyl-2-(2-hydroxy-1-naphthyl)propionitrile (I), which forms colorless crystals, m. p. 185-185.5°; it may be dissolved in 0.5% KOH and recovered by acidification. In the infrared spectrum we found frequencies for the CN group at about 2250 cm^{-1} and for the C=O group at about 1680 cm^{-1}. However, if the conditions are changed and the reaction is carried out at room temperature in a nitrogen atmosphere in a 1:9 water-dioxane mixture in presence of catalytic amounts of calcium oxide, the product is the imine of 1-phenacylnaphtho-[2,1-b]furan-2(1H)-one (II), a yellow substance, decomp. temp. 152-153°, which is an isomer of the substance (I); it is insoluble in alkali and may be readily prepared by boiling (I) in alcohol. In the infrared spectrum of (II) the CN frequency is absent and there is a somewhat displaced C=O frequency at about 1660 cm^{-1}. These results lead to the conclusion that the white substance (I) is a noncyclized form of the adduct, while (II) is the cyclized form. On hydrolysis with hydrochloric acid, (I) and (II) give the same product, 1-phenacylnaphtho-[2,1-b]furan-2(1H)-one (III), which was prepared also by the fusion of 3-benzoylacrylic acid with 2-naphthol.

We succeeded in decyclizing the naphthofuranone (III) by treating it with piperidine, as a result of which we isolated the piperidide of 3-benzoyl-2-(2-hydroxy-1-naphthyl)propionic acid. On being heated with 40% sodium hydroxide solution (III) is again decyclized with formation of the corresponding disodium salt, which, on being shaken with excess of dimethyl sulfate, gives the dimethylated product (in the infrared spectrum the C=O frequency is at about 1690 cm^{-1}). Prolonged heating of the disodium salt with 10% NaOH solution gives acetophenone and 2-naphthol. The latter indicates the addition of the naphthol at the double bond of 2-cyanovinyl phenyl ketone in the β-position to the C=O group, and not in the α-position, as otherwise in the hydrolytic cleavage it would be impossible for acetophenone and 2-naphthol to be formed simultaneously.



It is clear from our investigations that the carbonyl group in 2-cyanovinyl ketones polarizes the double bond more strongly than the CN group does.



EXPERIMENTAL

Addition of aniline and of N-methylaniline to 2-cyanovinyl ketones. To a solution of 0.1 mole of aryl 2-cyanovinyl ketone in the least possible amount of absolute methanol we added 0.1 mole of aniline or N-methylaniline. The reaction mixture was heated to the boil and then left for 3-4 hr at room temperature. The precipitate of 2-anilino-3-benzoyl- or 3-benzoyl-2-N-methylanilino-propionitrile was filtered off and washed with dry ether. 2-Cyanovinyl methyl ketone reacts with aniline on heating for 4-5 hr in equimolecular amounts in dry ether (see Table 1).

TABLE 1. $RCOCH{=}CHCN + NHR'C_6H_5 \rightarrow RCOCH_2CH(NR'C_6H_5)CN$

R	R'	Yield, %	M. p. (°C)	C %		H, %		N, %		Hal. %	
				found	calc.	found	calc.	found	calc.	found	calc.
CH_3	H	61.01	108-110 (from petroleum ether–acetone)	70.20	70.18	6.40	6.42	15.03	14.88	–	–
C_6H_5	H	75.88	131-132 (from methanol)	76.70	76.77	5.61	5.63	10.88	11.19	–	–
p-BrC_6H_4	H	64.00	151.5-152 (from alcohol)	58.33	58.37	3.86	3.98	8.72	8.51	23.79	24.27
o-ClC_6H_4	H	87.33	105-108 (from alcohol)	64.43	67.48	4.37	4.60	10.03	9.84	13.02	12.45
C_6H_5	CH_3	87.50	98.5-99.5 (from alcohol)	77.12	77.26	6.10	6.06	–	–	–	–

2-Anilinovinyl methyl ketone. To a solution of 0.42 g of sodium hydroxide in 30 ml of absolute methanol we added 1.3 g of 3-acetyl-2-anilinopropionitrile. The reaction mixture was left for 48 hr and then poured into water and dried over sodium sulfate; solvent was distilled off. The residue was slowly crystallizing mass, m. p. 79-81°. The yield of 2-anilinovinyl methyl ketone was 0.89 g (80.1%). After two crystallizations from 5:1 aqueous acetone it had m. p. 104-105°. The literature [16] has m. p. 103-104.5°. A mixture with a known sample melted without depression.

2-Anilinovinyl phenyl ketone. This was prepared by shaking 2 g of 2-anilino-3-benzoylpropionitrile with a solution of 0.5 g of sodium hydroxide in 100 ml of absolute alcohol. The yield was 1.6 g (89.8%); m. p. 140-142° (from alcohol). The literature [16] gives m. p. 140-141°.

Hydrolysis of 2-anilino-3-benzoyl- and 3-benzoyl-2-N-methylanilinopropionitriles. The nitrile (1 g) was dissolved, under cooling with water and ice, in 5 ml of 70% perchloric acid. The temperature of the mixture was gradually brought to that of the room, and after 20 minutes the solution was poured onto ice. The precipitate formed was carefully washed with cold water and dried. The yield of 2-anilino-3-benzoylpropionamide was 0.81 g (75.7%); m. p. 163° with decomp. (three times from alcohol). Found: C 71.51; H 6.07; N 10.44%. $C_{16}H_{16}O_2N$. Calculated: C 71.62; H 6.01; N 10.44%.

The yield of 3-benzoyl-2-N-methylanilinopropionamide was 0.8 g (75.4%); m. p. 142° (from aqueous alcohol). Found: 72.65; M 6.47; N 9.94%. $C_{17}H_{18}O_2N$. Calculated: C 72.34; H 6.38; N 9.93%.

Reaction of 3-benzoylacrylamide with aniline. A solution of 0.52 g of aniline in 5 ml of methanol was added to a suspension of 1.2 g of 3-benzoylacrylamide, prepared by the hydrolysis of 2-cyanovinyl phenyl ketone by the method described earlier [17], in 15 ml of absolute methanol. The reaction mixture was heated until the precipitate was completely dissolved and was left for one day at room temperature. The yield of 2-anilino-3-benzoylpropionamide was 1.45 g (84.3%); m. p. 161-162° (from alcohol), undepressed by admixture of the sample obtained in the preceding experiment.

Addition of sodium bisulfite to aryl 2-cyanovinyl ketones. To 0.1 mole of the 2-cyanovinyl ketone and a further 5% of this amount, dissolved in 100 ml of hot alcohol, we added 0.1 mole of $NaHSO_3$ as a 40% solution. The reaction mixture was left overnight. The precipitate formed was filtered off, washed with ether, dried, and crystallized from alcohol to which 1-2 drops of HCl were added; finally it was recrystallized from pure alcohol. The resulting sodium 2-aroyl-1-cyanoethanesulfonates generally contained one-half of a molecule of water of crystallization, which they lost when heated over P_2O_5 in a vacuum (Table 2).

TABLE 2. $RCOCH{=}CHCN + NaHSO_3 \rightarrow RCOCH_2CHCN$ (with SO_3Na on the CH)

R	Crystallization water	Decomp temp (°C)	Yield %	C (%) found	C (%) calc.	H (%) found	H (%) calc.	N (%) found	N (%) calc.	Hal (%) found	Hal (%) calc.
C_6H_5	$\frac{1}{2}H_2O$	237	95,5	44,44	44,44	3,10	3,33	4,87	5,18	—	—
C_6H_5	—	237	—	46,01	45,97	3,27	3,08	5,28	5,36	—	—
o-ClC_6H_4	$\frac{1}{2}H_2O$	213—216	95,4	39,68	39,40	2,63	2,62	4,75	4,59	12,26	11,62
o-BrC_6H_4	$\frac{1}{2}H_2O$	209—210	94,5	34,70	34,67	2,35	2,29	4,10	4,01	26,20	22,92
p-BrC_6H_4	$\frac{1}{2}H_2O$	290	94,2	34,49	34,67	2,42	2,29	—	—	—	—

Hydrolysis of sodium 2-benzoyl-1-cyanoethanesulfonate with hydrochloric acid. The salt (2 g) was refluxed with 25 ml of concentrated hydrochloric acid until the precipitate was almost completely dissolved. The solution was rapidly filtered through a porous filter. The crystals precipitated from the filtrate were filtered off. The yield of the sodium salt of 2-benzoyl-1-carboxyethanesulfonic acid was almost quantitative; decomp. temp. 299-300° when heated rapidly. Found: C 42.86; H 3.35%. $C_{10}H_9O_6SNa$. Calculated: C 42.85; H 3.21%.

In its infrared and ultraviolet spectra the product coincided with the previously described product of the reaction of 3-benzoylacrylic acid with sodium sulfite [6] after subsequent treatment with concentrated hydrochloric acid.

Reaction of 3-benzoylacrylic acid with sodium bisulfite. To a hot solution of 5 g of 3-benzoylacrylic acid we added 7.2 g of a 40% solution of sodium bisulfite. The reaction mixture was heated to the boil and then left

overnight. The precipitate formed was washed with alcohol on the filter. Yield 5 g (63.6%); decomp. temp. 298-302° (from alcohol with the addition of 1-2 drops of concentrated hydrochloric acid). A mixture with the above-described sample melted without depression; their infrared and ultraviolet spectra coincided.

Reaction of sodium 2-benzoyl-1-cyanoethanesulfonate with piperidine. To 2.79 g (0.01 mole) of sodium 2-benzoyl-1-cyanoethanesulfonate hydrate we added 500 ml of alcohol and 1.27 g (0.015 mole) of piperidine. The mixture was refluxed for 20 hr. At first the precipitate dissolved, and then a fine heavy precipitate of sodium bisulfite formed (it gave a reaction for SO_3^- with KIO_3 and starch-iodide paper). The filtrate was evaporated, and the residue was treated with water. The substance that remained undissolved by the water was phenyl 2-piperidinovinyl ketone; yield 12 g (55.81%); m. p. 90-92° (from methanol). The literature [14] gives m. p. 86-89°. A mixture with a known sample melted without depression.

Reaction of 2-cyanovinyl phenyl ketone with 2-naphthol. 2-Cyanovinyl phenyl ketone (3 g; 0.019 mole) and 2-naphthol (2.85 g; 0.019 mole) in a mixture of water (500 ml) and dioxane (50 ml) with an addition of 5 ml of a saturated solution of calcium hydroxide were set aside in a refrigerator for one week. The precipitate was filtered off and crystallized from dichloroethane. We obtained 3.2 g (55%) of 3-benzoyl-2-(2-hydroxy-1-naphthyl)propionitrile; m. p. 185-185.5° with decomp. (from dichloroethane). Found: C 79.67; H 5.22; N 4.69%. $C_{20}H_{15}NO$. Calculated: C 79.73; H 5.02; N 4.65%.

The substance may be dissolved by shaking it with 0.5% KOH and recovered unchanged by careful acidification with 10% hydrochloric acid (m. p. 185-185.5° with decomp.); the infrared spectrum coincided with that of the original substance.

A solution of 3 g (0.019 mole) of 2-cyanovinyl phenyl ketone and 5.6 g (0.039 mole) of 2-naphthol in a mixture of 9 ml of dioxane and 1 ml of water was saturated with nitrogen; 0.02-0.03 g of CaO was added as a fine powder. After 15-20 minutes the mixture crystallized out completely. The precipitate was filtered off, washed with a little dioxane, and dried in a stream of nitrogen. We obtained 4 g (69%) of the imine of 1-phenacylnaphtho[2,1-b]furan-2(1H)-one, m. p. 192° (from chloroform). Found: C 79.57; H 5.01; N 4.81%. $C_{20}H_{15}ON$. Calculated: C 79.73; H 5.02; N 4.65%.

Conversion of 3-benzoyl-2-(2-hydroxy-1-naphthyl)propionitrile into the imine of 1-phenacylnaphtho[2,1-b]-furan-2(1H)-one. 3-Benzoyl-2-(2-hydroxy-1-naphthyl)propionitrile (3 g) was boiled in 75 ml of alcohol for 90 min. When the solution was cooled, a dark-colored precipitate separated, and this was filtered off and dried; weight 2.1 g; m. p. 151-152° (decomp.). A mixture with the imine of 1-phenacylnaphtho[2,1-b]furan-2(1H)-one prepared earlier melted without depression.

Hydrolysis of 3-benzoyl-2-(2-hydroxy-1-naphthyl)propionitrile. The nitrile (2 g) was heated in a water bath for two hours with 25 ml of concentrated hydrochloric acid. The precipitate was filtered off; the yield of 1-phenacylnaphtho[2,1-b]furan-2(1H)-one was 1.9 g (94.5%); m. p. 196° (from CH_3NO_2). Found: C 79.27; H 4.71%. $C_{20}H_{14}O_3$. Calculated: C 79.45; H 4.67%.

Hydrolysis of the imine of 1-phenacylnaphtho[2,1-b]furan-2(1H)-one. The imine of 1-phenacylnaphtho[2,1-b]furan-2(1H)-one (2 g) was shaken for seven hours with 17 ml of 10% HCl. The precipitate was washed with alcohol and then crystallized from this solvent. The yield of 1-phenacylnaphtho[2,1-b]furan-2(1H)-one was 1.4 g (70%); m. p. 196-196.5° (from nitromethane). A mixture with the product of the preceding experiment melted without depression.

Reaction of 3-benzoylacrylic acid with 2-naphthol. A mixture of 5 g of 2-naphthol and 6.1 g of 3-benzoylacrylic acid was fused at 140°, and the temperature was then raised slowly to 170°. Liberation of water vapor was observed. The whole operation lasted for 20-25 minutes. When cool, the reaction mass was treated with ether. The undissolved precipitate of 1-phenacylnaphtho[2,1-b]furan-2(1H)-one was crystallized from nitromethane; yield 5.7 g (54.8%); m. p. 195°. Mixtures with samples from the last two experiments melted without depression.

Opening of the lactone ring of 1-phenacylnaphtho[2,1-b]furan-2(1H)-one. a) With piperidine. 1-Phenacylnaphtho[2,1-b]furan-2(1H)-one (1 g) was dissolved with heat in piperidine (1.2 ml). The mixture was cooled, and to the red gellike mass we added 8 ml of water; the precipitate was filtered off, washed with water, and dried. The yield of the piperidide of 3-benzoyl-2-(2-hydroxy-1-naphthyl)propionic acid was 1.28 g; m. p. 135° (from heptane). Found: C 77.26; H 6.50; N 3.35%. $C_{25}H_{25}O_3N$. Calculated: C 77.50; N 6.51; N 3.61%.

b) With 40% sodium hydroxide solution. 1-Phenacylnaphtho[2,1-b]furan-2(1H)-one (4 g) was heated in 40% NaOH (50 ml) for two hours. The precipitate was filtered off. The aqueous solution of the salt in water was made alkaline, and gradual addition was made of 1-2 ml of dimethyl sulfate (17 ml). The precipitate formed was filtered off, washed with water, and dried. The yield of dimethylated product was 3.1 g; m. p. 112.5-113° (from alcohol). Found: C 75.75; H 5.71%. $C_{22}H_{20}O_4$. Calculated: C 75.85; H 5.74%.

From the alkaline filtrate, after acidification, we isolated 0.45 g of the monomethylated product as the monohydrate; m. p. 142-143° (begins to soften at 115°). Found: C 71.65; H 5.70%. $C_{21}H_{18}O_4 \cdot H_2O$. Calculated: C 71.56; H 5.72%. After drying at 100° (10^{-3} mm), m. p. 158°. Found: C 75.18; H 5.47%. $C_{21}H_{18}O_4$. Calculated: C 75.44; H 5.38%.

Hydrolytic cleavage of the disodium salt. To the disodium salt obtained in method (b) of the preceding experiment from 4 g of 1-phenacylnaphtho[2,1-b]furan-2(1H)-one we added 200 ml of 10% sodium hydroxide solution. When the solution was heated, acetophenone distilled from the reaction mixture and was identified as its 2,4-dinitrophenylhydrazone; yield 1.8 g (45%). From the residue, by acidification and extraction with ether, we isolated 1 g (52.6%) of 2-naphthol.

SUMMARY

1. 2-Cyanovinyl ketones readily undergo addition with nucleophilic reagents at the double bond.

2. The addition of the nucleophilic grouping goes in the β-position to the carbonyl group. On this basis it is concluded that the double bond in 2-cyanovinyl ketones is more strongly conjugated with the carbonyl group and less strongly with the cyano group.

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VINYLTIN COMPOUNDS IN DIENE SYNTHESIS WITH CYCLONES

B. A. Arbuzov, L. A. Shapshinskaya, and M. I. Kudryavtseva

V. I. Ul'yanov-Lenin Kazan' State University
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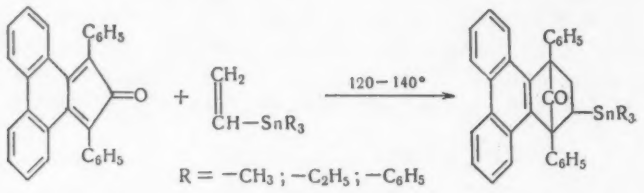
Original article submitted June 30, 1961

Cyclones, in undergoing the diene condensation with vinyl compounds of the type $CH_2=CHX$, in which vinyl is attached to oxygen, nitrogen, halogen, phosphorus, or metal, form unstable adducts. In the course of reaction these eliminate the endo-carbonyl bridge and the side chain containing the hetero atom with the result that the reaction products are phenylated benzenes [1-4]. Of all the known cyclones, the only exception is phencyclone [1,3-diphenyl-2H-cyclopenta[l-phenanthren-2-one], which in these reactions forms normal adducts containing an endo-carbonyl bridge.

With the object of making a further study of the behavior of cyclones in diene condensation with vinyl derivatives, and also of the possibility of obtaining new organometallic compounds by this reaction, we tried vinyltin compounds in diene condensation with cyclones. Vinyltin compounds became available for investigation only in 1957, when a simple and effective method was found for their preparation [5, 6]. We selected three vinyltin compounds $R_3SnCH=CH_2$, in which $R = -CH_3; -C_2H_5; -C_6H_5$. It was of interest to determine the relative ease with which these undergo diene condensation with cyclones.

Diene synthesis with vinyltin compounds was carried out in sealed tubes under carbon dioxide in a medium of dry benzene. The reaction temperature and time depended on the structures of the cyclone and the vinyltin compound. The end of the reaction was indicated by the disappearance of the characteristic color of the benzene solution of the cyclone.

As would be expected, the substance that most really underwent diene condensation with the vinyltin compounds was phencyclone. At 120-140° reaction with trimethyl- and triethyl-vinyltins was complete in 5-6 hr, but reaction with triphenylvinyltin required a much longer time. In all cases we obtained cyclic organotin compounds containing an endo-carbonyl bridge; they were white crystalline substances melting at about 200°.



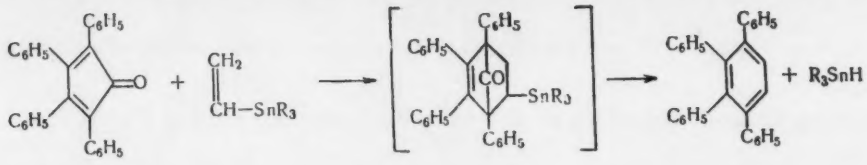
$R = -CH_3; -C_2H_5; -C_6H_5$

The diene condensations of tetracyclone (tetraphenylcyclopentadienone] and acecyclone [7,9] diphenyl-8H-cyclopent[a]acenaphthylen-8-one] with vinyltin compounds went with greater difficulty than in the case of phencyclone. Reaction was completed only after prolonged heating at 180-200°.

In no case did we succeed in obtaining the adduct of the diene condensation of tetracyclone or acecyclone with the vinyltin compound. It is probable that in the course of their formation there is immediate elimination of the endo-carbonyl bridge and the tin-containing side chain, as has been observed more than once in the diene condensation of cyclones with dienophiles of the type $CH_2=CHX$, in which X is not a carbon atom.

The only reaction product obtained was the corresponding phenylated benzene. In the reactions of tetracyclone with vinyltin compounds we obtained vic-tetraphenylbenzene, and in the reactions of acecyclone we obtained 2,3-(1,8-naphthylene)-1,4-diphenylbenzene [7, 10-diphenylfluoranthene]; these products were identified by mixture

melting point tests with the known hydrocarbons prepared by the diene condensation of tetracyclone and of acecyclone with dibromoethane [7]. With respect to their readiness to undergo diene condensation, the vinyltin compounds



$R_3SnCH=CH_2$; R = $-CH_3$; $-C_2H_5$; $-C_6H_5$) may be placed in the sequence: $CH_3 \rightarrow C_2H_5 > C_6H_5$.

After we had carried out this investigation there appeared a paper by Rothman and Becker [8] on the reaction between tetracyclone and triphenylvinyltin. They carried out the reaction in boiling nitrobenzene. As in our case, the reaction product was tetraphenylbenzene. When the reaction was carried out in bromobenzene, in addition to tetraphenylbenzene, they obtained 2,3-dihydrotetracyclone.

EXPERIMENTAL

Reaction of phencyclone with trimethylvinyltin. A mixture of 0.5 g of phencyclone, 0.5 g of trimethylvinyltin and 20 ml of dry benzene was heated in a sealed tube in an atmosphere of carbon dioxide for six hours at 120-127°. The color of the solution changed from dark green to yellow. The benzene solution was evaporated. The residue was treated with absolute alcohol, when yellowish crystals, m. p. 184-187°, were precipitated. After two crystallizations from alcohol with active charcoal treatments we obtained white crystals, m. p. 193-194°; yield 50% on the phencyclone. Found: Sn 20.41% [9]. $C_{34}H_{30}OSn$. Calculated: Sn 20.70%. The reaction product was 1,4-endocarbonyl-1,2,3,4-tetrahydro-1,4-diphenyl-2-(trimethylstannyl)triphenylene.

Reaction of phencyclone with triethylvinyltin. A mixture of 0.6 g of phencyclone, 0.5 g of triethylvinyltin, and 20 ml of dry benzene was heated in a sealed tube for ten hours at 120-130°. The further treatment was the same as in the preceding experiment. We obtained a white crystalline substance, m. p. 184-185°; yield 49% on the phencyclone. Found: Sn 19.50%. $C_{37}H_{36}OSn$. Calculated: Sn 19.29%. The reaction product was 1,4-endocarbonyl-1,2,3,4-tetrahydro-1,4-diphenyl-2-(triethylstannyl)triphenylene.

Reaction of phencyclone with triphenylvinyltin. A mixture of 0.56 g of phencyclone, 0.6 g of triphenylvinyltin and 25 ml of dry benzene was heated in a sealed tube for 43 hr at 140-150°. The further treatment was analogous to that in the above-described experiments. After several crystallizations from a mixture of alcohol and benzene with active charcoal treatments we obtained a white product, m. p. 253-254°. Found: Sn 15.30%. $C_{49}H_{36}OSn$. Calculated: Sn 15.63%. The reaction product was 1,4-endocarbonyl-1,2,3,4-tetrahydro-1,4-diphenyl-2-(triphenylstannyl)-triphenylene.

Reaction of tetracyclone with trimethylvinyltin. A mixture of 0.5 g of tetracyclone, 0.5 g of trimethylvinyltin, and 20 ml of dry benzene was heated in a sealed tube for 16 hr at 180-190°. The benzene solution was evaporated, and the residue was treated with alcohol. There was a fine pink precipitate, m. p. 175-178°. After several recrystallizations from a mixture of alcohol and acetone we obtained white crystals, m. p. 190-191°; yield 63.5% on the tetracyclone. A mixture of the product with vic-tetraphenylbenzene [7] melted without depression.

Reaction of tetracyclone with triethylvinyltin. A mixture of 0.5 g of tetracyclone, 0.5 g of triethylvinyltin, and 20 ml of dry benzene was heated at 190-200° for five hours. The treatment of the products was as in the preceding experiment. We obtained glistening white crystals, m. p. 190-191°; yield 52% on the tetracyclone. A mixture of the product with vic-tetraphenylbenzene melted without depression.

Reaction of acecyclone with trimethylvinyltin. A mixture of 0.5 g of acecyclone, 0.6 g of trimethylvinyltin, and 20 ml of dry benzene was heated at 170-190° for 20 hours and at 200-230° for ten hours. The characteristic blue color of the solution of acecyclone in benzene passed into dirty brown. The tube was opened, the benzene solution was evaporated, and the residue was treated with alcohol. There was a brown precipitate, which was carefully washed with cold alcohol and recrystallized from a mixture of alcohol and benzene. We obtained yellow crystals, m. p. 158-159°. The yield of product was only 18% on the acecyclone. A mixture with 7,10-diphenylfluoranthene prepared by the reaction of acecyclone with dibromoethane melted without depression.

Reaction of acecyclone with triphenylvinyltin. A mixture of 0.5 g of acecyclone, 0.56 g of triphenylvinyltin, and 25 ml of dry benzene was heated at 200-230° for 50 hours. The reaction products were treated exactly as in the

preceding experiment. We obtained a very small amount of yellow crystals, m. p. 158-159°. A mixture with 7,10-diphenylfluoranthene melted without depression.

SUMMARY

1. In diene condensations with cyclones, trimethylvinyltin reacts the most readily and triphenylvinyltin the least readily.

2. New cyclic organotin compounds were obtained as the result of the reaction of phencyclone with vinyltin compounds.

3. The reactions of vinyltin compounds with tetracyclone and with acecyclone occur with elimination of the endo-carbonyl bridge and the tin-containing side chain.

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PHOSPHORIC AND PHOSPHOROTHIOIC ESTERS CONTAINING HETEROCYCLIC GROUPS

COMMUNICATION 4. REACTION OF PHOSPHOROCHLORIDIC AND PHOSPHOROCHLORIDOTHIOIC COMPOUNDS WITH 2-AMINOPYRIDINE

B. A. Arbuzov, V. M. Zoroastrova, and M. P. Osipova

A. M. Butlerov Chemical Institute, V. I. Ul'yanov-Lenin Kazan State University

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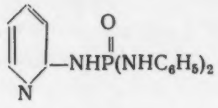
The object of our work was the study of the chemical and biological properties of phosphoric and phosphorothioic derivatives containing 2-aminopyridine and 2-aminopyridine 1-oxide groupings.

The reaction of dialkyl phosphorochloridates with 2-aminopyridine was studied by Lugovkin and Arbuzov [1]. The reaction was carried out under severe conditions without solvent and was accompanied by the liberation of alkyl chloride and hydrogen chloride and the evolution of much heat. As a result the authors obtained the alkylation product of 2-aminopyridine. The alkylating action of dialkyl phosphorochloridates was established also in the case of aniline, 2-naphthylamine, and diphenylamine.

We carried out the reaction of dialkyl phosphorochloridates and of dialkyl phosphorochloridothioates with 2-aminopyridine 1-oxide under milder conditions: at room temperature or with heating in a water bath. The experiments were carried out in ether or benzene solution. In this way we prepared some phosphoric amido esters: dimethyl, diethyl, diisopropyl, and diisobutyl 2-pyridylphosphoramidates and the phosphoric triamide



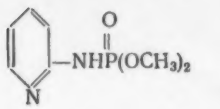
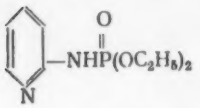
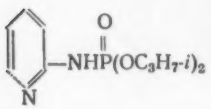
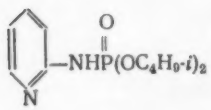
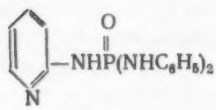
The physical properties of the compounds obtained are presented in the table.

All the above-listed products are crystalline substances, soluble in the usual organic solvents and to different extents in water. As a rule the compounds with the smaller organic groups are more soluble in water than those with the larger organic groups. To characterize the substances synthesized we prepared their picrates, the physical constants of which are given in the table. The amido esters synthesized were hydrolyzed with 1:1 hydrochloric acid. Phosphoric acid was determined as phenylhydrazine phosphate.

For diethyl and diisopropyl 2-pyridylphosphoramidates we determined the infrared spectra. In these spectra there were two intense absorption bands at 1598 and 1498 cm^{-1} and also an intense band at 1581 cm^{-1}, which overlapped the band at 1598 cm^{-1} and showed the presence of the pyridine ring [2]. An intense peak at 1307 cm^{-1} confirmed the presence of the Ar—NH— grouping. In the P=O absorption region there was a peak at 1255 cm^{-1}. In the spectrum of diisopropyl 2-pyridylphosphoramidates in the region of the CH deformation vibrations there was a doublet at 1384, 1374 cm^{-1}, which is characteristic of the isopropyl group. Thus, the spectrum data confirm the structure of the dialkyl phosphoramidates synthesized.

To determine the mechanism of the alkylation of amines by dialkyl phosphorochloridates, first observed by Lugovkin and Arbuzov [1] for the case of 2-aminopyridine and other amines, we carried out special experiments on the thermal decomposition of the amido esters obtained. Dimethyl and diisopropyl 2-pyridylphosphoramidates were heated in Arbuzov flasks to 220-225°. In the decomposition products we found 2-dimethylaminopyridine and 2-isopropylaminopyridine, which were identified in the form of picrates.

TABLE

Formula	M p. (°C)	Yield (%)*	M.p. of picrate (°C)
	108-109 (colorless prisms from mixture of benzene and petroleum ether)	59	(orange prisms)
	86-88 (colorless needles from water)	75	130—131
	135-136 (colorless needles from aqueous alcohol)	64,4	151—152
	75-76 (colorless prisms from heptane)	67,4	
	217-218 (colorless prisms from aqueous alcohol)	67	

* The yields are those of the crude products.

It was proposed to prepare analogous amido esters containing a pyridine 1-oxide grouping by the action of dialkyl phosphorochloridates on 2-aminopyridine 1-oxide or by the oxidation of the already prepared dialkyl 2-pyridylphosphoramidates. However, in neither case did our experiments give the desired results. Since 2-aminopyridine 1-oxide is very sparingly soluble in most organic solvents, with the exception of chloroform, the experiments were carried out in the latter solvent. The remaining conditions were the same as in the reactions with 2-aminopyridine. The reactions proceeded with formation of 2-aminopyridine 1-oxide hydrochloride (in the theoretical amount). When solvent was vacuum-distilled from the filtrate, a thick reddish-yellow mass remained in the flask, and this could not be crystallized and did not distill without decomposition. Attempts were made to isolate the desired products in the form of picrates. However, this also did not give satisfactory results.

We proposed also to prepare the analogous dialkyl 2-pyridylphosphoramidothioates. With this object we carried out the reactions of 2-aminopyridine with dimethyl and diethyl phosphorochloridothioates under the same conditions as in the case of dialkyl phosphorochloridates. The reactions proceeded with slight evolution of heat and the formation of 2-aminopyridine hydrochlorides. We did not succeed in isolating the reaction products in the pure state.

The dialkyl 2-pyridylphosphoramidates that we synthesized (R = CH_3-, C_2H_5-, i-C_3H_7-, i-C_4H_9-) were investigated by Prof. B. L. Mazur at Kazan' Medical Institute for bactericidal properties toward some kinds of bacteria. Preliminary experiments showed that these compounds have no bactericidal properties.

EXPERIMENTAL

Reaction of Dimethyl Phosphorochloridate with 2-Aminopyridine. To an ethereal solution of 3 g of dimethyl phosphorochloridate (2:1). There was a slight rise in temperature (from 21° to 26°). The mixture was heated in a water bath under reflux for 3.5 hours. At the end of the reaction the ethereal solution was poured from the thick yellow mass, which was found to be the hydrochloride of 2-aminopyridine, the melting point of which is 86°. On evaporation of the ether a precipitate formed that amounted to 2.4 g (59%). Crystals obtained by recrystallization from a mixture of benzene and petroleum ether had m.p. 108-109°*. The substance formed colorless prisms; it dissolved in ethyl acetate, ether, benzene, methanol, and ethanol; it also dissolved readily in water. Found: P 15, 76; 15.36%. $C_7H_{11}N_2PO_3$. According to the analysis the product was dimethyl 2-pyridylphosphoramidate.

* On recrystallization from benzene or petroleum ether (70-100°) the solutions should not be brought to the boil, but only to about 50-60°, as otherwise an oil is precipitated which does not dissolve in benzene.

Hydrolysis. A mixture of 0.2 g of the product and 8 ml of 1:1 HCl was refluxed for eight hours. The solution was evaporated on a water bath with repeated addition of water to remove HCl; phenylhydrazine was added to the residue. A precipitate formed on cooling, and this was washed free from phenylhydrazine with a mixture of benzene and petroleum ether. Recrystallization from aqueous alcohol gave colorless scales characteristic for phenylhydrazine phosphate; m.p. 155°, undepressed by admixture of known phenylhydrazine phosphate.

Picrate. When alcoholic solutions of our product and of picric acid were mixed, there was a precipitate. The picrate obtained had m.p. 149-150°. Found: P 7.06%. $C_{13}H_{14}N_5PO_{10}$. Calculated: P 7.19%.

Reaction of Diethyl Phosphorochloridate with 2-Aminopyridine. A mixture of 3 g of 2-aminopyridine and 2.75 g of diethyl phosphorochloridate (2:1) in 50 ml of dry benzene was refluxed for two hours. A yellow oil fell to the bottom of the flask, and the benzene solution was poured off from this. On removal of benzene in a vacuum, crystals were precipitated. The weight of crude product was 2.7 g (75%). Recrystallization from water gave colorless needles, melting at 86-88° and readily soluble in ether, benzene, alcohols, and hot water. Found: P 13.30, 13.38%. $C_9H_{15}O_3N_2P$. Calculated: P 13.47%. Hence, the product was diethyl 2-pyridylphosphoramidate.

Picrate. This was prepared as described above: yellow prisms, m.p. 130-131°. Found: P 6.89%. $C_{15}H_{18}N_5PO_{10}$. Calculated: P 6.75%.

Reaction of Diisopropyl Phosphorochloridate with 2-Aminopyridine. To 3.1 g of 2-aminopyridine and 3.5 g of triethylamine in 50 ml of dry ether at room temperature we added 7 g of diisopropyl phosphorochloridate (1:1) in an equal volume of ether. The temperature of the reaction mixture remained almost without change. The mixture was refluxed in a water bath for 3.5 hours; when it had cooled, a precipitate of triethylamine hydrochloride was filtered off. On evaporation of ether, a precipitate formed in the filtrate; weight 5.8 g (64.4%). After being crystallized from aqueous alcohol the product melted at 135-136°; it formed colorless needles, readily soluble in ether, alcohols, benzene, and toluene, but not so soluble in water. Found: P 11.74; 11.94%. $C_{11}H_{19}N_2PO_3$. Calculated: P 12%. According to the analysis the product was diisopropyl 2-pyridylphosphoramidate. Its hydrolysis with hydrochloric acid gave phosphoric acid (phenylhydrazine phosphate, m.p. 155°). By treatment of part of the hydrolysis products with alkali we obtained 2-aminopyridine, m.p. 57°. A mixture with pure 2-aminopyridine melted without depression.

Picrate. This was prepared as described above; m.p. 151-152°. Found: P 6.60%. $C_{17}H_{22}N_5PO_{10}$. Calculated: P 6.36%.

Reaction of Diisobutyl Phosphorochloridate with 2-Aminopyridine. A mixture of 2.35 g of 2-aminopyridine and 2.85 g of diisobutyl phosphorochloridate (2:1) was boiled in 50 ml of ether for three hours. The ethereal solution was decanted from the oil (2-aminopyridine hydrochloride) and left overnight; a precipitate was formed. The weight of crude product was 2.4 g (67.4%). Recrystallization from heptane gave large almost colorless (with yellowish tinge) prisms, m.p. 75-76°. The product was readily soluble in benzene, toluene, chloroform, methanol, and ethanol, but not so soluble in water. Found: P 11.12; 11.17%. $C_{13}H_{23}N_2PO_{10}$. Calculated: P 10.83%. The product was diisobutyl 2-pyridylphosphoramidate.

Reaction of N,N'-Diphenylphosphorodiamidic Chloride with 2-Aminopyridine. A mixture of 1 g of 2-aminopyridine and 1.5 g of N,N'-diphenylphosphorodiamidic chloride [3] (2:1) in dioxane was refluxed in a water bath for two hours. At the end of the reaction the solution was decanted from the oil precipitated (1.2 g; 67%). After being crystallized from aqueous alcohol the product had m.p. 217-218°. The substance was soluble in alcohol, benzene, toluene, and dioxane, very soluble in butanone, and sparingly soluble in water. Found: C 61.25; 61.66; H 5.25; P 10.30%. $C_{17}H_{17}N_4PO$. Calculated: C 62.9; H 5.28; P 9.56%.

Thermal Decomposition of Dimethyl 2-Pyridylphosphoramidate. Dimethyl 2-pyridylphosphoramidate (2.5 g) was placed in a small Arbuzov flask fitted with a thermometer that reached almost to the bottom. The flask was heated in a bath of Wood's metal. At a bath temperature of 135° the contents of the flask melted, and at 180° the temperature inside the flask rose rapidly to 197°. In the further heating of the bath to 230° the temperature inside the flask was lower than the bath temperature by 12-15°. Heating was continued for 5-7 minutes. The contents of the flask formed a dark-colored glassy mass. An oily liquid (0.15 g) was distilled off into a receiver, and from this a picrate was prepared. After recrystallization from acetone we isolated glistening yellow prisms, m.p. 181.5-182°, which was found to be the picrate of 2-dimethylaminopyridine. A mixture with the picrate of synthesized 2-dimethylaminopyridine melted at 180-182°.

When the glassy residue in the reaction flask was treated with ice water, treated with caustic alkali solution, and extracted with ether, we isolated a dark-colored thick liquid, which contained traces of the original amide ester.

We prepared a picrate of m.p. 151-152°. An attempt to distill the liquid at 1 ml did not give satisfactory results: we obtained a black resin.

Thermal Decomposition of Diisopropyl 2-Pyridylphosphoramidate. Diisopropyl 2-pyridylphosphoramidate (1.5 g) was heated in an Arbuzov flask. At a bath temperature of 220-225° a vigorous boiling set in, and on the walls of the flask there appeared a yellow oily liquid with an aminelike odor, which collected in the siphon of the flask and was extracted with a pipet (0.08 g). A dark-colored glassy product remained in the flask. The liquid that distilled off did not contain phosphorus. On addition of alcoholic picric acid there was a precipitate of a picrate of m.p. 173-175°, which corresponded analytically to the picrate of the alkylation product of 2-aminopyridine. Found: C 45.59; H 4.35%. $C_8H_{12}N_2 \cdot C_6H_3N_3O_7$. Calculated: C 46.01; H 4.13%.

The glassy mass was dissolved in aqueous alkali and extracted with ether. The ether extract was dried with sodium sulfate. After removal of ether an oily liquid with an aminelike odor remained in the flask (0.38 g); in this we detected 2-aminopyridine. The picrate prepared from this had m.p. 215-217°, undepressed by admixture of 2-aminopyridine picrate.

Reaction of Dimethyl Phosphorochloridothioate with 2-Aminopyridine. To an ethereal solution of 3.2 g of 2-aminopyridine we added an ethereal solution of 2.8 g of dimethyl phosphorochloridothioate (2:1). There was a slight rise in temperature, and a yellow oil was precipitated on the bottom of the flask. The liquid part was decanted from the oily layer and set aside for crystallization. When solvent was evaporated off there remained a sticky thick yellow mass, which we were unable to crystallize. An experiment carried out with heating in a water bath gave analogous results.

Reaction of Diethyl Phosphorochloridothioate with 2-Aminopyridine. A mixture of 1g of 2-aminopyridine and 1 g of diethyl phosphorochloridothioate (2:1) in ether was refluxed in a water bath for two hours. On removal of ether under reduced pressure there was a precipitate, which was found to be 2-aminopyridine. Under these conditions reaction did not go. An experiment carried out in benzene solution with heating in a water bath gave a noncrystallizing product, from which were unable to isolate any pure substance.

Reaction of Diethyl Phosphorochloridate with 2-Aminopyridine 1-Oxide. Experiment 1. To 6.7 g of 2-aminopyridine 1-oxide and 6.16 g of triethylamine in 30 ml of dry benzene we added 10.05 g of diethyl phosphorochloridate (1:1). The temperature of the reaction mixture rose from that of the room to 73°. The mixture was heated for 2.5 hours at the boiling point of the solvent. The precipitate was filtered off. Benzene was distilled off from the liquid part, which was then vacuum-distilled. As the result of distillation in a high vacuum we obtained a little of a substance of b.p. 50-53° (0.15 mm) and n^{20}_D 1.4265 (its composition remained unknown). The remainder decomposed when heated further; there remained a solid black resin (5.5 g) in the distilling flask.

Experiment 2. To 2.2 g of 2-aminopyridine 1-oxide in chloroform we added 1.73 g of diethyl phosphorochloridate (2:1). The temperature rose from 18° to 26°. The reaction mixture was refluxed in a water bath for two hours. The precipitate formed was filtered off (1.2 g) and was found to be 2-aminopyridine 1-oxide hydrochloride, m.p. 158-159°. Found: Cl 24.16; 24.27%. C_5H_7NOCl. Calculated: Cl 24.2%.

After the removal of chloroform there remained a thick reddish-brown noncrystallizing liquid in the flask. On addition of alcoholic picric acid there was a yellow precipitate. Attempts to purify the picrate by recrystallization from glacial acetic acid, acetone, butanone, dioxane, benzene, and alcohol were unsuccessful. We could not obtain a picrate with a sharp melting point.

Reaction of Diisopropyl Phosphorochloridate with 2-Aminopyridine 1-Oxide. A mixture of 2.2 g of 2-aminopyridine 1-oxide and 2 g of diisopropyl phosphorochloridate (2:1) in 100 ml of freshly distilled dry chloroform was refluxed for two hours. When the mixture was cool, the precipitate was filtered off (1.1 g of 2-aminopyridine 1-oxide hydrochloride). The filtrate was vacuum-evaporated. To the thick liquid that remained, which did not crystallize out, we added alcoholic picric acid. There was a yellow precipitate, from which we did not succeed in isolating a pure picrate.

Oxidation of Diisopropyl 2-Pyridylphosphoramidate. A mixture of 1 g of the amido ester and 6 ml of 11.8% monoperoxyphthalic acid in dry ether was left overnight. The precipitate formed was filtered off (0.65 g; m.p. 132-149°). We were unable to obtain a product of sharp melting point by recrystallization from the usual organic solvents.

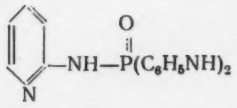
From the filtrate, after evaporation of ether, we again obtained a mixture of crystalline products (0.55 g) which melted over a wide range of temperature (132-157°). Attempts to separate these products by the use of various solvents were unsuccessful.

SUMMARY

1. Reaction of phosphorochloridic esters with 2-aminopyridine gave some phosphoramidic esters, and the picrates of these were isolated.

2. In the thermal decomposition of these amido esters alkylation products of 2-aminopyridine were isolated.

3. By the reaction of $(C_5H_5NH)_2P(=O)Cl$ with 2-aminopyridine we synthesized the phosphoric triamide



$$C_5H_4N\text{—}NH\text{—}P(=O)(C_5H_5NH)_2$$

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REACTIONS OF CHLORO(TRIMETHYLSILOXY)SILANES

K. A. Andrianov and N. V. Delazari

Institute of Heteroorganic Compounds, Academy of Sciences, USSR
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Chloro(trimethylsiloxy)silanes are of considerable interest for the preparation of polyorganosiloxanes of linear structure with an open packing of the molecular chains. However, these compounds have been inadequately studied in reactions with nucleophilic and electrophilic reagents. In a previous investigation [1] it was shown that dichlorobistrimethylsiloxysilane reacts with water in absence of acceptors for hydrogen chloride not only with replacement of halogen by hydroxyl, but also with elimination of the trimethylsiloxy group with formation of insoluble products close to SiO_2 in composition. The high reactivity of the trimethylsiloxy groups in dichlorobistrimethylsiloxysilane, leading to the cleavage of an Si–O–Si linkage, is unusual. In this connection it was of interest to study other reactions of compounds containing silicon-attached trimethylsiloxy. Experiment showed that tristrimethylsiloxysilanol does not react with tetrabutoxytitanium or stannic chloride after long heating in presence of an acceptor, such as pyridine or ammonia. In all cases, on distillation of the reaction products the reactants were recovered unchanged. When tristrimethylsiloxysilanol is heated in presence of hydrogen chloride, dimer is not formed, but the starting substance is recovered unchanged. Great interest was presented by a study of the aminolysis of chloro(trimethylsiloxy)silanes. When dichlorobistrimethylsiloxysilane was treated with ammonia in a benzene medium at room temperature, two products were formed: bistrimethylsiloxysilanediamine and 1,3-bistrimethylsiloxy-1,3-disilazanediamine. These two compounds were formed by the reaction:

$$3[(CH_3)_3SiO]_2SiCl_2+NH_3 \longrightarrow [(CH_3)_3SiO]_2Si(NH_2)_2+$$

$$+[(CH_3)_3SiO]_2\text{—}\underset{\underset{NH_2}{|}}{Si}\text{—}NH\text{—}\underset{\underset{NH_2}{|}}{Si}\text{—}[(CH_3)_3SiO]_2 \qquad (I)$$

(II)

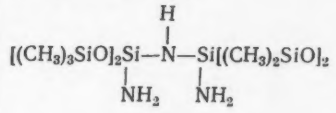
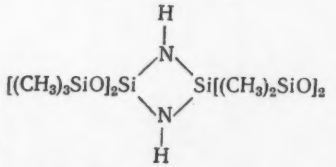
The yield of bistrimethylsiloxysilane diamine was 53.1% and that of 1,3-bistrimethylsiloxy-1,3-disilazanediamine was 22.2%. Unlike the hydrolysis reaction, the aminolysis reaction was not accompanied by the formation of complex insoluble polymers, which indicates no elimination of the trimethylsiloxy group. Study of the properties of bistrimethylsiloxysilanediamine showed that prolonged heating at 212-304° resulted in the liberation of ammonia and the formation of a crystalline substance of m.p. 104°. Analyses and molecular weight determination showed that (III) is a product of the condensation of bistrimethylsiloxysilanediamine:

$$2[(CH_3)_3SiO]_2Si(NH_2)_2 \longrightarrow [(CH_3)_3SiO]_2\,\underset{\text{(III)}}{\overset{\overset{N}{|}}{\overset{N}{\diagup\ \diagdown}}}\,Si\,\underset{\overset{N}{|}}{\overset{\overset{N}{\diagup\ \diagdown}}{\diagdown\ \diagup}}\,Si\,[(CH_3)_3SiO]_2$$

In proof, of the structure of the product (III) we carried out a confirmatory synthesis: 1,3-bistrimethylsiloxy-1,3-disilazanediamine was heated for 25 hours at 280-344°. We obtained a product of m.p. 103° and molecular weight 435. Analysis corresponded to (III). In aminolysis reactions we did not observe the elimination of a trimethylsiloxy group and the formation of insoluble products. The properties of the new compounds obtained are presented in the table.

Investigation of the reaction of chlorotristrimethylsiloxysilane with sodium with the object of preparing sodium tristrimethylsiloxysiloxide showed that the reaction goes at above 150°, when hydrogen starts to be liberated at an.

TABLE

Substance	Formula	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	*MR* found	*MR* calc.	Yield (%)
Bistrimethylsiloxysilanediamine	$[(CH_3)_3SiO]_2Si(NH_2)_2$	51—53(3)	1,4057	0,9066	64,43	64,04	53,1
1,3-Bistrimethylsiloxy-1,3-disilazanediamine		117—119(3)	1,4119	0,9338	122,28	122,66	22,2
2,4-Bistrimethylsiloxycyclodisilazane		180—183(4) m.p. 103	—	—	—	—	25,5
Tristrimethylsiloxysilylamine	$[(CH_3)_3SiO]_3SiNH_2$	65—67(3,5)	1,3932	0,8755	84,81	84,51	61,6
Sodium Tristrimethylsiloxysiloxide	$[(CH_3)_3SiO]_3SiONa$	—	—	—	—	—	17,9
Tetrakis(tristrimethylsiloxysiloxy)-titanium	$\{[(CH_3)_3SiO]_3SiO\}_4Ti$	223—225(1,5)	1,4201	0,9623	341,9	338,2	57,3

appreciable rate. It was shown that in the course of the reaction not only sodium tristrimethylsiloxysiloxide was formed, but also tetrakistrimethylsiloxysilane. Reaction went in accordance with the scheme:

$$10(CH_3)_3SiO]_3SiOH + Na \xrightarrow{150^\circ} NaOH +$$

$$+ 2[(CH_3)_3SiO]_3SiONa + 6[(CH_3)_3SiO]_4Si$$

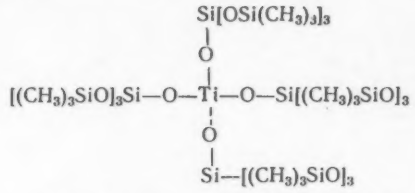
The formation of tetrakistrimethylsiloxysilane is associated with the cleavage of the Si–O–Si linkage under the conditions of reaction.

As a result of the reaction we isolated sodium tristrimethylsiloxysiloxide in 17.9% yield and tetrakistrimethylsiloxysilane in 53% yield. When tristrimethylsiloxysilanol is heated for a long time with titanium tetrachloride there is no reaction (the starting substances are recovered unchanged), whereas a double-decomposition reaction leads to the formation of tetrakis(tristrimethylsiloxysiloxy)titanium in accordance with the scheme:

$$4[(CH_3)_3SiO]_3SiONa + TiCl_4 \longrightarrow \{[CH_3)_3SiO]_3SiO)_4Ti$$

The cleavage of the Si–O–Si linkage is not then observed.

It is interesting that, despite the high molecular weight of tetrakis(tristrimethylsiloxysiloxy)titanium and its high inorganic content (80.7%), this substance is a mobile liquid, sp. gr 0.9623 and b.p. 223-225° (1.5 mm). Such properties are to be explained by the cruciform structure of tetrakis(tristrimethylsiloxysiloxy)titanium



in which the inorganic part of the molecule is framed with methyl groups, which ensure weak interactions between the molecules. The cruciform structure of the molecule does not allow close packing, which is confirmed by the low specific gravity of the compound.

EXPERIMENTAL

Preparation of Bistrimethylsiloxysilanediamine and 1,3-Bistrimethylsiloxy-1,3-disilazanediamine. A 500-ml three-necked flask fitted with stirrer, thermometer, reflux condenser, dropping funnel, and tube for the bubbling of ammonia was charged with 150 ml of dry benzene. We added 42 g (0.15 mole) of dichlorobistrimethylsiloxysilane (b.p. 170-173°) in 50 ml of dry benzene from the dropping funnel with continuous stirring and passage of ammonia at room temperature (22°). There was a white precipitate of NH_4Cl. Toward the end of the reaction the temperature of the reaction mass rose to 41°. Ammonia was passed further for 90 minutes. The precipitate was filtered off; benzene was distilled off at the water pump. The residue (31.2 g) was fractionated at the oil pump. Two products were isolated: The first, b.p. 51-53° (3 mm), amounted to 19.1 g (53.1%); $n^{20}D$ 1.4057; nD_2^0 1.4057; d_4^{20} 0.9066; Found MR 64.43; Calculated MR 64.04. Found: C 30.42; H 9.15; Si 34.90; N 11.61%. $C_6H_{22}Si_3O_2N_2$. Calculated: C 30.3; H 9.24; Si 35.38; N 11.76%. The second b.p. 117-119° (3 mm) amounted to 7.7 g (22.2%); nD^{20} 1.4119; d_4^{20} 0.9338; Found: MR 122.28; Calculated MR 122.66. Found: C 31.47; H 9.06; Si 36.35; N 8.13%. $C_{12}H_{41}Si_6O_4N_3$. Calculated: C 31.41; H 8.94; Si 36.62; N 9.16%.

Preparation of 2,4-Bistrimethylsiloxycyclodisilazane. 1,3-Bistrimethylsiloxy-1,3-disilazanediamine (7.7 g) was heated under reflux for eight hours at 212-304°. The transparent needles precipitated amounted to 1.2 g (25.5%); m.p. 104°. Found: C 32.83; H 8.69; Si 37.99; N 5.95%; mol. wt. 433. $C_{12}H_{33}O_4Si_6N_2$. Calculated: C 32.61; H 8.58; Si 38.01; N 6.33%; mol. wt. 442.

Preparation of Tristrimethylsiloxysilylamine. A 200-ml three-necked flask fitted with stirrer, thermometer, reflux condenser, dropping funnel, and tube for the bubbling of ammonia was charged with 100 ml of dry benzene. We added 20 g (0.061 mole) of chlorotristrimethylsiloxysilane (b.p. 200-202°) in 30 ml of dry benzene from the dropping funnel with continuous stirring and passage of ammonia at room temperature (22°). There was a white precipitate of NH_4Cl. Toward the end of the reaction the temperature rose to 36°. Ammonia was passed further for 90 minutes. The precipitate was filtered off; benzene was distilled off at the water pump. The residue (17.4 g) was

was fractionated at the oil pump. We isolated 11.6 g (61.6%) of a product of b.p. 65-67° (3.5 mm); n^{20}_D 1.3932; d_4^{20} 0.8755; Found: MR 84.81; Calculated MR 84.51. Found_ C 35.56; H 9.50; Si 35.87; N 4.62%. $C_9H_{29}O_3Si_4N$. Calculated: C 34.76, H 9.32; Si 36.08; N 4.5%.

Preparation of Sodium Tristrimethylsiloxysiloxide. A 100-ml three-necked flask fitted with stirrer, reflux condenser, and thermometer was charged with 40 g (0.124 mole) of tristrimethylsiloxysilanol. Sodium (0.9 g; 0.039 mole) was added in portions to the reaction mixture at 120°. The reaction proceeded at 150-170° for 15 hours. The amount of unchanged sodium was 0.41 g. After one day at room temperature there was a precipitate of 6.9 g (17.9%) of clear regular rhombic crystals, soluble in benzene and xylene. Found: C 32.99; H 8.53; Si 32.7; Na 6.85%. $C_9H_{27}Si_4O_4Na$. Calculated: C 32.42; H 8.11; Si 33.6; Na 6.85%.

The crystals were filtered off, and the filtrate was distilled. We isolated 20.4 g (53%) of tetrakistrimethylsiloxysilane; b.p. 74-76° (4 mm); n^{20}_D 1.3875; d_4^{20} 0.8660. For $[(CH_3)_3SiO]_4Si$ [2]: b.p. 91° (9 mm); n^{20}_D 1.3865; d_4^{20} 0.8750.

Preparation of Tetrakis(tristrimethylsiloxysiloxy)titanium. A 50-ml three-necked flask fitted with stirrer, reflux condenser, and thermometer was charged with 2.27 g (0.0068 mole) of sodium tristrimethylsiloxysiloxide in 20 ml of dry xylene. At 132° 0.39 g (0.0017 mole) of titanium tetrachloride in 10 ml of dry xylene was added dropwise from the dropping funnel. There was a white precipitate of NaCl. Heating with stirring was continued for 5 hr 40 min. The precipitate was filtered off, and the xylene was distilled off at the water pump. Fractionation of the residue gave 1.3 g (57.3%) of a product having: b.p. 223-225° (1.5 mm); n^{20}_D 1.4201; d_4^{20} 0.9623; Found MR 341.9; Calculated MR 338.2. Found: C 33.40; H 8.32; Si 33.23; Ti 3.82%. $C_{36}H_{108}Si_{16}O_{16}Ti$. Calculated: C 33.41; H 8.35; Si 34.67; Ti 3.78%.

SUMMARY

1. The aminolysis of chloro(trimethylsiloxy)silanes proceeds with replacement of halogen by an amino group without elimination of the trimethylsiloxy group.

2. Double decomposition of sodium tristrimethylsiloxysiloxide with titanium tetrachloride leads to the formation of a compound of cruciform structure, namely tetrakis(tristrimethylsiloxysiloxy)titanium.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

GAS-PHASE REACTION OF BROMO- AND CHLORO-SILANES CONTAINING SILICON-ATTACHED HYDROGEN WITH SOME ORGANIC BROMO COMPOUNDS AND WITH ALKYLCHLORO-BENZENES

E. A. Chernyshev, N. G. Tolstikova, and E. F. Bugerenko

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR
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In a study of the mechanism of the high-temperature reaction to halosilanes containing silicon-attached hydrogen with organic halo compounds, which proceeds along two parallel routes

$$R_nHal_{3-n}SiH + R'Hal' \begin{cases} \longrightarrow R_nHal_{3-n}SiR' + HHal' & (C) \\ \longrightarrow R_nHal_{3-n}SiHal' + R'H & (R) \end{cases}$$

we showed [1] that the molar ratio between the condensation products C and the reduction products R is determined both by the nature of the halosilane and by the nature of the organic halide. It was found that replacement of chlorine atoms in trichlorosilane by organic groups favors reduction in the value of C/R. Thus, C/R for the reaction between $HSiCl_3$ and C_6H_5Cl is 2.4, whereas the value for reaction between CH_3SiHCl_2 and C_6H_5Cl under the same conditions is 1.0. It was of interest to investigate what effect on the change in the proportions of condensation and reduction product would be had by the replacement of chlorine atoms in the halosilane $HSiHal_3$ by another halogen, in particular by bromine. With this object we investigated the reactions of tribromosilane with bromobenzene, with 1-bromonaphthalene, and with allyl bromide. As aromatic reactants we took aryl bromides, instead of aryl chlorides, so as to avoid an exchange reaction of the type

$$\rangle C-Cl + \rangle Si-Br \rightleftarrows \rangle C-Br + \rangle Si-Cl$$

which would make the isolation of reaction products in an individual pure state difficult.

The values of C/R for the reactions investigated are given in Table 1. For comparison, in Table 1 we give the values of C/R for the reaction of trichlorosilane with the same organic bromides which we obtained earlier [1].

TABLE 1. Values of C/R for the Reactions of $HSiBr_3$ and $HSiCl_3$ with Some Organic Bromides

Organic bromide	Value of C/R	
	for reaction with $HSiBr_3$	for reaction with $HSiCl_3$
		0
C_6H_5Br	0.24	1.1
α-$C_{10}H_7Br$	1.55	.1
$CH_2=CH-CH_2Br$	0.14	–

The data in Table 1 show that replacement of chlorine atoms by bromine in the halosilane favors condensation. From this it follows that the proportion of condensation and reduction products is affected not only by the electronegativity of the atoms or groups attached to silicon in the silane, but also their size (steric factor) and possibly also the structure of their electron shells. As would be expected, as a result of the lower degree of ionic character of the Si–H bond in tribromosilane, as compared with the same bond in trichlorosilane, tribromosilane is more reactive in high-temperature reactions with organic halides. Thus, at 580° with a time of contact of 30 seconds $HSiCl_3$ reacts with chlorobenzene with a conversion of 70-75%, whereas $HSiBr_3$ undergoes quantitative (98-99%) conversion. Because of the fairly high tendency of 1-bromonaphthalene to undergo the condensation reaction, the yield of tribromo-1-naphthylsilane in the reaction between α-$C_{10}H_7Br$ and $HSiBr_3$ is 60%. The yields of tribromophenyl- and allyltribromosilanes are lower (17.5% and 12.5%, respectively).

Investigation of the reactivity of alkylchlorobenzenes in high-temperature reaction with hydride silanes showed that it varies over an extremely narrow range depending on the position of the alkyl substituent relative to chlorine atom [2]. Since, under the conditions of high-temperature condensation, isomerization of alkylchlorobenzenes is not observed and replacement of chlorine by the silyl group always occurs in that position of the ring which contained [1-6], it would be expected that in the reaction of hydride silanes with a mixture of alkylchlorobenzene isomers as in the original reactants. This view was confirmed experimentally. We studied the high-temperature gas-phase reaction of trichlorosilane and of dichloromethylsilane with chlorotoluenes, chlorocumenes, and 1-chloro-4-t-butylbenzene. This part of the work was carried out with the object of comparing the possibilities of synthesizing tolyl-, (ethylphenyl)-, and cumenyl-chlorosilanes by gas-phase high-temperature condensation and by older methods, namely liquid-phase reaction of hydride chlorosilanes with alkylbenzenes or alkylchlorobenzenes. As a result of the approximately equal reactivities of alkylchlorobenzenes in their reactions with hydride chlorosilanes at temperatures above 600°, in all cases the proportions of the resulting ortho, meta, and para isomers of (alkylphenyl)trichlorosilanes and (alkylphenyl)dichloromethylsilanes are, according to spectrum data (Raman spectra), approximately the same as in the original alkylchlorobenzenes.

Tolyl-, (ethylphenyl)-, and cumenyl-chlorosilanes were prepared earlier by the liquid-phase reaction of hydride chlorosilanes with alkylbenzenes or alkylchlorobenzenes in accordance with the schemes [7-9]

$$(CH_3)_nCl_{3-n}SiH + RC_6H_5 \longrightarrow RC_6H_4Si(CH_3)_nCl_{3-n} + H_2 (n=0,1)$$

$$HSiCl_3 + RC_6H_4Cl \longrightarrow RC_6H_4SiCl_3 + SiCl_4 + H_2.$$

Comparative data on the yields of organosilicon monomers prepared by various methods are given in Table 2.

TABLE 2. Yields of (Alkylaryl)chlorosilanes Prepared by Various Methods

(Alkylaryl)chlorosilane	Yield (% on original silane)		
	gas-phase reaction of $HSiCl_3$ or CH_3SiHCl_2 with aryl halide	liquid-phase reaction of $HSiCl_3$ or CH_3SiHCl_2	
		with alkylbenzene	with alkylchlorobenzene
$CH_3C_6H_4SiCl_3$	50	44	63
$C_2H_5C_6H_4SiCl_3$	43	24	57
$i\text{-}C_3H_7C_6H_4SiCl_3$	35	20	56.5
$CH_3C_6H_4SiCH_3Cl_2$	30	32	–
$C_2H_5C_6H_4SiCH_3Cl_2$	23	32	–
$i\text{-}C_3H_7C_6H_4SiCH_3Cl_2$	21	36	–

In the gas-phase reaction of 1-chloro-4-t-butylbenzene with trichlorosilane we obtained trichloro(p-t-butylphenyl)silane in 27% yield. Under the same conditions, from 1-chloro-4-t-butylbenzene and dichloromethylsilane dichloromethyl(p-t-butylphenyl)silane was formed in 21% yield. However, in this method twice as much silane is consumed as in the other two. Comparison of the gas-phase reaction of hydride silanes with aryl chlorides with the liquid-phase reaction of hydride silanes with alkylbenzenes shows that the former gives the best yields when trichlorosilane is used, and the latter when dichloromethylsilane is used. In the gas-phase reaction of hydride silanes with alkylcholorbenzenes at temperatures above 600-620° a considerable residue is formed in the still, and elementary analysis shows that this contains silicon and hydrolyzable chlorine as well as carbon and hydrogen.

EXPERIMENTAL

Reaction of Tribromosilane with Organic Bromides. The reactor was an empty quartz tube heated in an electric tube furnace. The temperature was maintained constant within ± 3° over the whole length of the tube. The reactants were introduced with an automatic spray at a rate which ensured that the time in the reaction zone was in the range 27-30 seconds. In all cases the ratio of the amounts of reactants RBr : $HSiBr_3$ was 2 : 1. Beyond the reactor the products passed through a condenser and were collected in a receiver. Beyond the receiver there was a trap cooled in a mixture of solid carbon dioxide and acetone. The condensate was fractionated through a column, and the products were analyzed as described previously [3]. The experimental results are given in Table 3.

TABLE 3. Results of the Reaction of Tribromosilane with Organic Bromides

Reactants	Tribromosilane obtained	Temp in reaction zone (°C)	Yield %	B.p. in °C (in p in mm)	n_D^{20}	d_4^{20}	Br content (%) calc.	Br content (%) found
$C_6H_5Br+HSiBr_3$	$C_6H_5SiBr_3$	580	17,5	98—99 (3)	1,5994	2,0242	69,60	69,32 69,48
α-$C_{10}H_7Br+HSiBr_3$	α-$C_{10}H_7SiBr_3$	580	60	147—150 (2)	1,6689	1,9090	60,75	60,38 60,54
$CH_2=CHCH_2Br+HSiBr_3$	$C_3H_5SiBr_3$	540	12,5	184—185 (750) 59—62 (7)	1,5350	2,0612	77,75	77,80 77,27

Reaction of Trichlorosilane and of Dichloromethylsilane with Chlorotoluenes. A mixture of the isomeric chlorotoluenes was prepared by the chlorination of toluene in the dark at 10-15° in presence of $FeCl_3$. For further investigation we took the fraction of b.p. 158-162°. According to spectrum data (Raman spectra) the proportions of isomers were: ortho about 60%, para about 40%, meta about 10%. We carried out the reaction in the same apparatus as that used in the study of the reaction of organic bromides with tribromosilane. The molar ratio $RCl:HSiCl_3$ was 1:1. The experiments were carried out at 600-680° with a time of contact of 30 seconds. The value of C/R was about 2.5. However, the amount of silicon tetrachloride formed increased threefold with rise in temperature from 600° to 680° because of increased pyrolysis of trichlorosilane. The yield of trichlorotolylsilane at 605° was 38%, at 650° was 50%, and at 680° was 38%. The resulting mixture of isomeric trichlorotolylsilanes had the following properties: b.p. 210-215° (750 mm); n^{20}_D 1.5212; d_4^{20} 1.2878. Found: Cl 47.05; 47.10%. $C_7H_7SiCl_3$. Calculated: Cl 47.50%. Spectrum analysis showed that the mixture of trichlorotolylsilanes had approximately the same composition as the original mixture of chlorotoluenes. The reaction of chlorotoluenes with dichloromethylsilane was carried out under the same conditions with the same proprotions of reactants as in the case of trichlorosilane. At 590° the yield of dichloromethyltolylsilanes was 30% and at 620° it was 27%. The value of C/R was 1.45. The resulting dichloromethyltolylsilane had the following properties: b.p. 215-219° (760 mm); n^{20}_D 1.5156; d_4^{20} 1.1227. Found: Cl 32.85; 33.10%. $C_8H_{10}SiCl_2$. Calculated: Cl 34.30%. Spectrum analysis showed the same proportions of isomers in the dichloromethyltolylsilanes as in the original chlorotoluenes.

Reaction of Trichlorosilane and of Dichloromethylsilane with Chloroethylbenzenes. A mixture of isomeric chloroethylbenzenes was prepared by the alkylation of chlorobenzene with ethyl bromide in presence of aluminum chloride. For the further investigation we took the fraction of b.p. 178-186° (760 mm). The proportion of isomers in the mixture was established by spectrum analysis: meta about 60%, para about 25%, ortho about 15%. The experiments on the reaction of trichlorosilane with chloroethylbenzenes were carried out under the same conditions as those with chlorotoluenes. The value of C/R was 2.3. At 610° the yield of trichloro(ethylphenyl)silanes was 43%, and at 645° it was 30%. At 650° with a contact time of 11 seconds the yield of trichloro(ethylphenyl)silanes was 41%. The resulting trichloro(ethylphenyl)silane had the following properties: b.p. 225-232° (760 mm); n^{20}_D 1.5250; d_4^{20} 1.2375. Found: Cl 43.90; 44.10. $C_8H_9SiCl_3$. Calculated: Cl 44.55%. Spectrum analysis (Raman spectra) showed that the proportions of isomers in the trichloro(ethylphenyl)silane was approximately the same as in the original chloroethylbenzene. The reaction of chloroethylbenzenes with dichloromethylsilane was carried out under the same conditions as in the case of trichlorosilane. The temperatures were 560° and 645°. In the first case the yield of dichloro(ethylphenyl) methylsilane was 20.5%, and in the second 23.2%. The value of C/R was 1.24. The properties of the resulting dichloro (ethylphenyl)methylsilane were: b.p. 228-230° (750 mm); n^{20}_D 1.5095; d_4^{20} 1.1212. Found: Cl 31.90; 32.10%. $C_9H_{12}SiCl_2$. Calculated: Cl 32.3%. Raman spectrum analysis indicated the same proportion of isomers as in the original chloroethylbenzene.

Reaction of Trichlorosilane and of Dichloromethylsilane with Chlorocumenes. For the reactions we used the mixture of isomeric chlorocumenes obtained by the chlorination of cumene in presence of $FeCl_3$; it had the properties: b.p. 192-195° (750 mm); n^{20}_D 1.5138; d_4^{20} 1.0331. The mixture consisted mainly of the para isomer with 30% of ortho and meta isomers. The reaction of chlorocumene with trichlorosilane was carried out at 610° with a contact time of 40 seconds and a reactant ratio of 1:1. The value of C/R was 2.2. The yield of trichlorocumenylsilane was 35%. This product had the following properties: b.p. 88-93° (3 mm); n^{20}_D 1.5203; d_4^{20} 1.2212. Found: Cl 40.58, 40.26%. $C_9H_{11}SiCl_2$. Calculated: Cl 41.20%. The Raman spectrum showed that the product was mainly the para isomer. The reaction of

chlorocumene with dichloromethylsilane was carried out under the same conditions as in the case of trichlorosilane; the temperature was 540°. The value of C/R was 1.2. Dichlorocumenylmethylsilane was obtained in 21% yield; it had the following properties: b.p. 88-91° (4.5 mm); n_D^{20} 1.5148; d_4^{20} 1.1248. Found: Cl 30.10; 30.44%. $C_{10}H_{14}SiCl_2$. Calculated: Cl 30.05%. The spectrum of the product showed that this contained a predominating amount of the para isomer.

Reaction of Trichlorosilane and of Dichloromethylsilane with chloro-t-butylbenzene. 1-Chloro-4-t-butylbenzene was synthesized by the method of [10] and had m.p. 24°. The reaction of 1-chloro-4-t-butylbenzene with trichlorosilane was carried out at a reactant ratio of 1:1 and with a contact time of 30 seconds. At 550° the yield of trichloro(p-t-butylphenyl)silane was 20%, and at 600° it was 27%. The value of C/R was 1.45. When the reaction was carried out at 650° with a contact time of 11 seconds there was considerable resinification and the yield of the desired product was 13%. Trichloro(p-t-butylphenyl)silane had the following properties: b.p. 85-87° (3 mm); n^{20}_D 1.5312; d_4^{20} 1.2291; found MR 67.37; calculated MR 67.76. Found: Cl 39.84; 39.90%. $C_{10}H_{13}SiCl_3$. Calculated: Cl 40.60%.

The reaction of 1-chloro-4-t-butylbenzene with dichloromethylsilane (reactant ratio 1:1; contact time 30 seconds) was carried out at 500°. Under these conditions the yield of dichloromethyl(p-t-butylphenyl)silane was 21%. The value of C/R was 1.2. At 560° there was already resinification, and the yield of the desired product fell to 5%. Dichloromethyl(p-t-butylphenyl)silane had the following properties: b.p. 116° (4 mm); n^{20}_D 1.5215; d_4^{20} 1.1090. Found: MR 67.87; Calculated MR 68. 10. Found: Cl 29.50; 29.10%. $C_{11}H_{16}SiCl_2$. Calculated: Cl 28.80%.

The spectrum analysis of the original substances and the products synthesized was carried out by L. A. Leites, to whom the authors express their deep gratitude.

SUMMARY

1. The gas-phase reaction of tribromosilane with organic bromides leads to a higher molar ratio of condensation products to reduction products (C/R) than the reaction of organic bromides with trichlorosilane under the same conditions.

2. The high-temperature reaction of mixtures of alkylchlorobenzene isomers with chlorosilanes containing silicon-attached hydrogen leads to the formation of (alkylphenyl)chlorosilanes containing the same proportion of isomers in yields of 20.50%.

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REPLACEMENT OF A MERCURY ATOM ATTACHED TO A SATURATED CARBON ATOM BY HALOGEN

COMMUNICATION 3. REACTION OF BENZYLMERCURY CHLORIDE WITH IODINE IN CARBON TETRACHLORIDE

I. P. Beletskaya, O. A. Reutov, and T. P. Gur'yanova

M. V. Lomonosov Moscow State University

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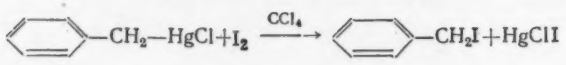
Earlier we reported on a study of the kinetics of the electrophilic replacement of the mercury residue by halogen in benzylmercury chloride in a series of polar solvents [1, 2]. In the present paper we report our results on the reaction of benzylmercury chloride with iodine in a carbon tetrachloride medium



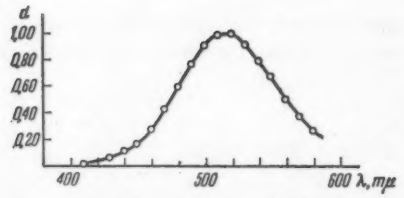


Fig. 1. Graduation curve $\underline{d} = f(\lambda)$ for carbon tetrachloride solution of iodine; concentration of iodine $c_{0I_2} = 2 \cdot 10^{-3}$ mole/liter.

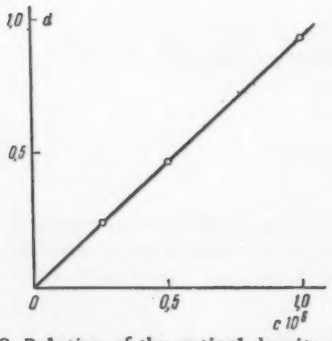


Fig. 2. Relation of the optical density of an iodine solution to its concentration; $\underline{d} = f(\underline{c})$.

The reaction is photochemical, so its kinetics were studied under constant illumination by a stabilized light source. The measurements were carried out spectrophotometrically with an SF-4 spectrophotometer; the rate of reaction was followed by the change in the optical density of the iodine solution at $\lambda =$ 520 mμ. In this region the mercury compound and the reaction products do not absorb. The graduation curve $\underline{d} = f(\lambda)$ for iodine solutions of concentration $c_{0I_2} = 2 \cdot 10^{-3}$ mole/liter, and also in excess of the organomercury compound. In the selected range of concentrations carbon tetrachloride solutions of iodine obey the Lambert-Beer law (Fig. 2), so that instead of the ratio c_0/c we shall in future use the corresponding ratio of optical densities.

EXPERIMENTAL

Carbon tetrachloride was purified by the method given in [3]. A solution of benzylmercury chloride in carbon tetrachloride was added with stirring to a carbon tetrachloride solution of iodine. The reaction mixture was poured into the cylindrical cell of the spectrophotometer and placed in a constant source of light. The illumination was provided by a 150-w filament lamp in a circuit containing a latr and a stabilizer (the p.d. across the latr was 82.5 v). The distance from the lamp to the cell was 25 cm. Every 5 minutes the cell was placed in the spectrophotometer and the optical density of the solution was measured (not more than 15-20 seconds was required for each measurement).

The experimental results on the change in the optical density of the solution with time for different original concentrations are given in Table 1. The measurements were carried out at 25-26°.

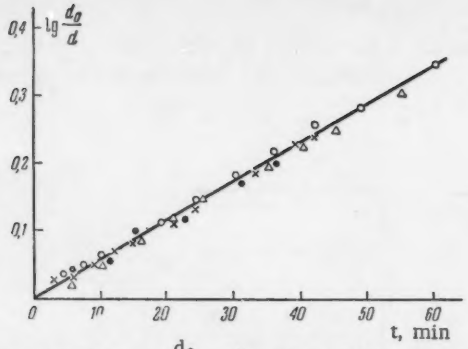


Fig. 3 Relation $\log \frac{d_0}{d} = f(\tau)$ for different original concentration reagents: $c_0 = 1 \cdot 10^{-3}$(O); $c_0 = 0.5 \cdot 10^{-3}$ (Δ); $c_{0RHgX} = 0.5 \cdot 10^{-3}$, $c_{0I_2} = 1 \cdot 10^{-3}$(□); $c_{0RHgX} = 0.5 \cdot 10^{-2}$, $c_{0I_2} = 1 \cdot 10^{-3}$ (×).

The rate constant of the reaction satisfies a first-order equation:

$$k_1 = \frac{1}{\tau} \ln \frac{c_0}{c}$$

With change in the original concentrations of the reactants the value of the half-exchange period remains constant, as can be seen from the graph of the relation

$$\lg \frac{d_0}{d} = f(\tau)$$

(Fig. 3). It will be seen from the experimental data (Table 1) that a tenfold increase in the concentration of the organomercury salt does not result in change in reaction rate. It follows that, with over-all first-order kinetics, the reaction is of first order with respect to iodine and of zero order with respect to benzylmercury chloride ($k_1 = 1.3 \cdot 10^{-2}$ min^{-1}).

TABLE 1

$C_0 = 1 \cdot 10^{-3}$ mole/liter		$C_0 = 0.5 \cdot 10^{-3}$ mole/liter		$C_{0I_2} = 1 \cdot 10^{-3}$ mole/liter $C_{0RHgX} = 1 \cdot 10^{-2}$		$C_{0I_2} = 1 \cdot 10^{-3}$ mole/liter $C_{0RHgX} = 0.5 \cdot 10^{-3}$	
t,min	d	t,min	d	t,min	d	t,min	d
4	0,361	5	0,207	6	0,355	3	0,365
7	0,350	10	0,190	11	0,345	6	0,359
10	0,339	15	0,178	15	0,324	9	0,345
15	0,311	20	0,167	22	0,298	12	0,334
19	0,301	25	0,156	31	0,263	15	0,325
24	0,279	30	0,146	36	0,246	18	0,309
30	0,257	35	0,138	46	0,234	21	0,302
36	0,236	40	0,130	52	0,234	24	0,286
42	0,214	45	0,123			27	0,264
49	0,203	50	0,116			30	0,256
60	0,175	55	0,108			36	0,239
67	0,154	60	0,104			39	0,229
74	0,147	65	0,098			42	0,224
		70	0,091			45	0,214

We studied the effect of the intensity of the irradiation on the rate of the process. The experiments were carried out under the above-described conditions with the use of neutral filters, for which the relative transmittances I (%) were determined. The corresponding experimental results are given in Table 2.

From the data in Table 2 we constructed a graph of the relation $\log \frac{d_0}{d} = f(\tau)$ (Fig. 4). There is a linear proportionality between the reaction rate and the intensity of illumination. The graph of the relation $k_1 = f(I)$ is given in Fig. 5.

Because of difficulties of method we did not succeed in checking the action of peroxides on the reaction rate. Reaction was not inhibited by additions of hydroquinone and m-dinitrobenzene. Addition of 1% by volume of ether had no effect on the rate of the process.

From the results it follows that the reaction probably proceeds by a two-stage mechanism. In the first stage, which determines the kinetics of the process as a whole, one molecule of iodine takes part. It is possible that in this stage there occurs the photochemical breakdown of this molecule into radicals or its photochemical initiation:

$$I_2 \xrightarrow{h\nu} 2I; \quad I_2 \xrightarrow{h\nu} I_2^*.$$

In the rapid stage of the reaction there occurs interaction with the organomercury molecule and formation of the final products

$$C_6H_5CH_2HgCl + 2I^{\cdot} \longrightarrow C_6H_5{-}CH_2I + HgClI$$

It is still difficult to state anything definite about this fundamental act in the reaction of iodine with benzylmercury chloride. It is known only that, as shown by special experiments, benzyl iodide is formed quantitatively in the reaction.

TABLE 2

$C_0 = 1 \cdot 10^{-3}$ mole/liter, I = 100		$C_0 = 1 \cdot 10^{-3}$ mole/liter, I = 61.3		$C_0 = 1 \cdot 10^{-3}$ mole/liter, I = 44.8		$C_0 = 1 \cdot 10^{-3}$ mole/liter, I = 34.2	
t, min	d	t, min	d	t, min	d	t, min	d
5	0,498	5	0,486	5	0,453	5	0,500
10	0,466	10	0,474	10	0,447	10	0,494
15	0,430	15	0,457	15	0,441	15	0,488
20	0,410	20	0,442	20	0,419	20	0,465
25	0,370	26	0,419	25	0,409	25	0,453
30	0,339	30	0,408	30	0,393	30	0,449
35	0,333	35	0,396	35	0,380	35	0,443
40	0,321	40	0,380	40	0,369	40	0,441
45	0,295	45	0,372	45	0,354	45	0,428
50	0,279	50	0,363	50	0,346	50	0,423
55	0,269	55	0,344	55	0,336	55	0,415
60	0,250	60	0,330	60	0,326	60	0,400
65	0,241	65	0,325	69	0,306		
70	0,231	70	0,318				
75	0,216	75	0,301				
80	0,204	85	0,285				
85	0,196	90	0,279				
90	0,187						
95	0,177						
$k_1 = 11,5 \cdot 10^{-3}$ min^{-1}		$k_1 = 7,2 \cdot 10^{-3}$ min^{-1}		$k_1 = 5,7 \cdot 10^{-3}$ min^{-1}		$k_1 = 3,9 \cdot 10^{-3}$ min^{-1}	

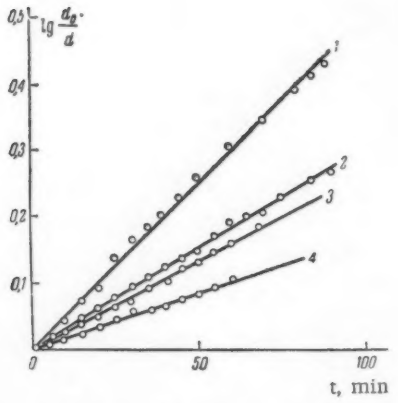


Fig. 4. Graph of the relation $\log \frac{d_0}{d} = f(\tau)$, obtained at various degrees of illumination: 1) 100%; 2) 61.3%; 3) 44.8%; 4) 34.2%.

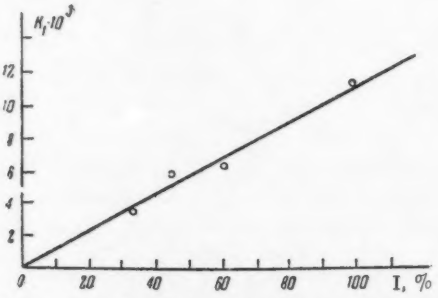
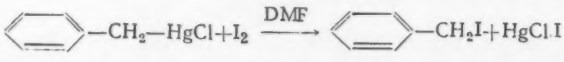


Fig. 5. Relation of the first-order rate constant to the relative degree of illumination.

The reaction of benzylmercury chloride was studied also in a polar medium, namely N,N-dimethylformamide (DMF)



The rate was measured spectrophotometrically at $\lambda = 450$ mμ (the relation $\underline{d} = f(\lambda)$ is given in Fig. 6) at a concentration of reactants of $1 \cdot 10^{-3}$ moles/ml. Reaction in the cold in the dark went at an immeasurably low rate. The conditions of measurement were therefore similar to those described above for carbon tetrachloride. However, change in the optical density of the solutions may be associated not only with the disappearance of iodine in the reaction, but also with the possible formation of a complex of iodine with the mercuric chloride liberated in the reaction,

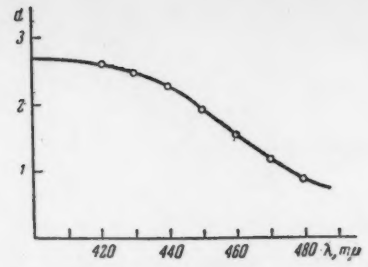


Fig. 6. Relation $\underline{d} = f(\underline{c})$ for solutions of iodine in N,N-dimethylformamide.

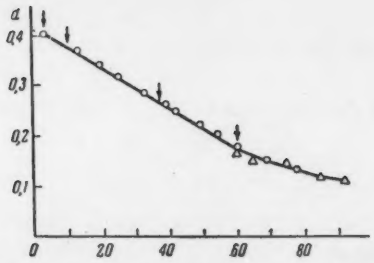


Fig. 7. Change in optical density with time for the reaction of benzylmercury chloride with iodine in N,N-dimethylformamide. The circles refer to moments of time when the discontinuation of illumination retards the process, and the triangles refer to moments of time when the process goes at the same rate in the dark as in the light.

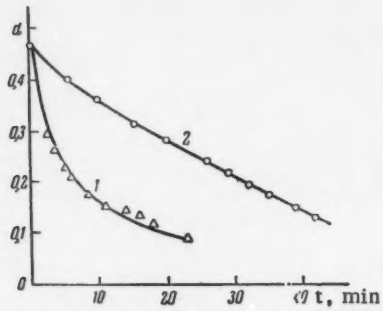


Fig. 8. Change in the optical density of solutions for reaction in N,N-dimethylformamide at 50° in presence (1) and in absence (2) of peroxides.

which was confirmed in control experiments*. The suggestion that under these conditions the reaction, because of the formation of the complex, goes by two parallel mechanisms, radical (photochemical) and electrophilic, was checked in the following way: at definite moments of time the illumination was removed and the cell containing the reaction mixture was placed in the spectrophotometer; it was then found that up to definite moment of time cutting off of the illumination stopped the reaction almost entirely; then we had a state of partial retardation; and, finally, from a certain moment of time (shown in Fig. 7) the reaction went at just the same rate in the dark as in the light. It is probable that from this moment benzylmercury chloride reacts not with a free molecule of iodine, but with a complex of the type $I_2 \cdot HgClI$ with a consequent change in the reaction mechanism.

It is interesting that the reaction of benzylmercury chloride with iodine in N,N-dimethylformamide may be initiated not only photochemically, but also thermally. We measured the rate of this reaction in the dark at 50° (the measurements were made spectrophotometrically in a thermostated cell). It was shown that under these conditions the addition of benzoyl peroxide greatly accelerates the process. The appropriate data on the change of optical density with time for reactant concentrations of $1 \cdot 10^{-3}$ mole/ml at 50° in presence and in absence of peroxide are given in Fig. 8.

SUMMARY

1. The kinetics of the reaction of benzylmercury chloride in carbon tetrachloride were studied.

2. The reaction is of the first order (first with respect to iodine and zero with respect to the organomercury compound).

3. In N,N-dimethylformamide, unlike carbon tetrachloride, the reaction mechanism is mixed. Additions of benzoyl peroxide accelerate the reaction.

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3. Organic Solvents [in Russian] (Moscow, 1958), p. 383.

*Because of this it is impossible to make quantitative calculations and the results have a qualitative character. It is also impossible to study the kinetics of the reaction in the ultraviolet region because the regions in which organomercury compounds and iodine absorb coincide.

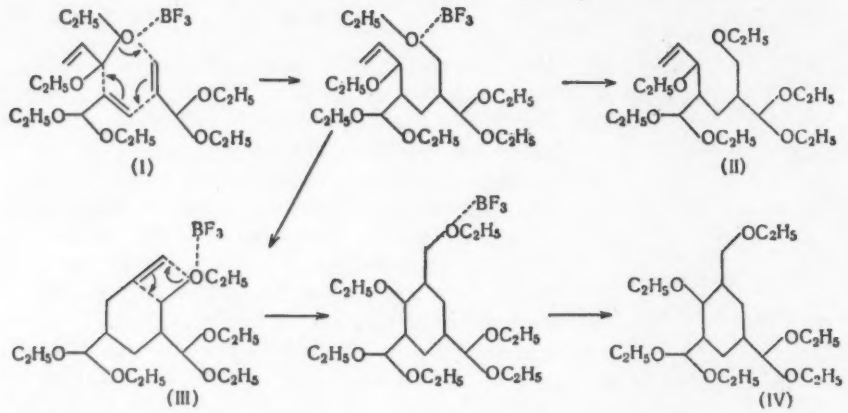
CHEMISTRY OF ACETALS

COMMUNICATION 9. MECHANISM OF THE TRIMERIZATION OF ACROLEIN ACETAL

S. S. Yufit and V. F. Kucherov

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR
Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk,
No. 12, pp. 2183-2184, December, 1961
Original article submitted July 6, 1961

On the basis of the proof of the structure of the trimer of acrolein diethyl acetal (II) we expressed the view that its formation proceeds via the quasi-aromatic intermediate complex (I) with cyclic electron transfer [1]

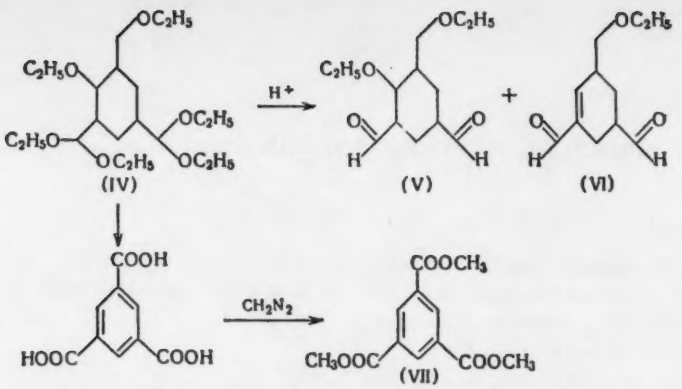


If this view is correct, then in the trimer (III) there may be intramolecular cyclization due to the spatial proximity of the ether group activated with boron trifluoride with the double bond. In the reaction products there should then be the isomeric cyclic trimer, which can be formed from the intermediate complex (III) [2].

As a result of a study of the high-boiling fraction of the trimerization product we isolated an individual substance of b.p. 146-148° (0.1 mm) and $n^{20}D$ 1.4472, which in molecular weight and elementary analysis corresponded to the composition $C_{21}H_{42}O_6$ and was an isomer of the previously described acyclic trimer (II). Found: C 64.80; 64.66; H 10.60; 10.79%. $C_{21}H_{42}O_6$. Calculated: C 64.58; H 10.84%. It was found that this product was incapable of actalytic hydrogenation, and its infrared and Raman spectra confirmed the absence of double bonds. According to oxime-formation results, this new trimer contained two acetal groupings and was therefore a dialdehyde diacetal in which the remaining two oxygen atoms were present as ordinary ether groups.

These data already lead us to the view that this trimer has the cyclic structure (IV). When it was treated with 2,4-dinitrophenylhydrazine in an acid medium, we isolated two hydrazones: One of these had m.p. 123° (from alcohol) and λ_{max} = 365.5 mμ; in elementary analysis it corresponded to the bisdinitrophenylhydrazone of the saturated dialdehyde (V). Found: C 49.71; 49.79; H 4.79; 4.49; N 18.89; 19.04%. $C_{25}H_{30}O_{10}N_8$. Calculated: C 49.90; H 4.90; N 18.60%.

The second hydrazone formed red crystals of m.p. 171-174° (from a mixture of ethyl acetate and petroleum ether); in analysis it corresponded to the bisdinitrophenylhydrazone of the unsaturated dialdehyde (VI). Found: N 19.85; 20.10%. $C_{23}H_{24}O_9N_8$. Calculated: N 20.5%. The same hydrazone was the main product formed from the products of the acid hydrolysis of the original trimer (IV)



For final proof of the structure of the cyclic trimer (IV) it was subjected to dehydrogenation over Pd/C at 320°, and the product was oxidized with chromium trioxide in acetic acid. We then isolated an aromatic acid, whose methyl ester was found to be identical with trimethyl trimesate (VII) (mixture m.p. and ultraviolet spectrum).

These results give direct confirmation of the presence of a cyclohexane ring in the trimer (IV), and they permit us to conclude that the trimerization of acrolein diethyl acetal does in fact pass through a cyclic intermediate state in accordance with the scheme given above. We discovered that the yield of the trimer (IV) is greatly increased in comparison with that of the noncyclic trimer (II) when the trimerization is carried out below −60°. This may be explained on the view that at low temperature more favorable conditions are created for the formation of the intermediate oriented complex (III) because of the low kinetic energy of the molecule.

SUMMARY

The structure of the cyclic product formed by the action of boron trifluoride on acrolein diethyl acetal is proved. This results confirm the scheme proposed earlier for the trimerization of the acetal.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

β-DICARBONYL COMPOUNDS

COMMUNICATION 13. CHEMICAL PROPERTIES OF MELDRUM'S ACID

S. I. Zav'yalov

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR
Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk,
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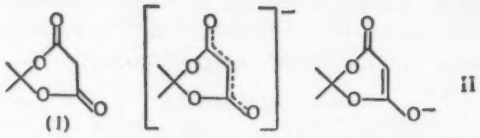
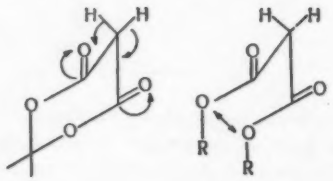
Original article submitted July 12, 1961

Meldrum's acid (isopropylidene malonate) (I) is one of the β-dicarbonyl compounds that does not conform to Claisen's rule relating to the parallelism between acidity and enolizability. In spite of its strongly marked acidic properties (pK 5.1) [1], in the undissociated state isopropylidene malonate exists only in the diketo form (absence of the maximum for the enol in the ultraviolet spectrum) [2]. Like the anions of other β-dicarbonyl compounds, the anion of Meldrum's acid shows considerable absorption in the ultraviolet and so must contain a conjugated system of bonds (II) [2].

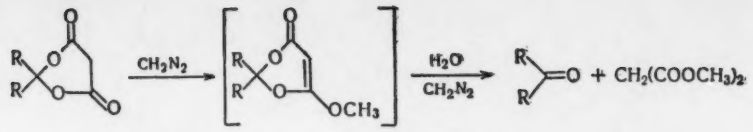


The high acidity of isopropylidene malonate is probably due to the relatively high rigidity of the m-dioxane ring, which favors the conjugation of C—H and C—C bonds. However, this important steric factor is insufficient for the enolization of the alkoxycarbonyl group. Malonic ester itself has not only low enolizability, but also feeble acidity, because the conformation in which the hydrogen and the carbonyl are close must here be energetically unfavorable because of the repulsion of the alkoxy groups.

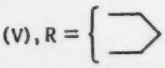


Because of its structural peculiarities, Meldrum's acid occupies an intermediate position between malonic ester and cyclic β-diketones of the 1,3-cyclohexanedione type; a study of its chemical behavior therefore presents great interest. The literature on Meldrum's acid [1] mainly considers its hydrolytic cleavage, and other typical reactions of β-diketones are examined to a less extent. In the present work we have studied the behavior of Meldrum's acid in reactions with diazomethane, piperidine, formaldehyde, nitrous acid, permanganate, and hydrogen peroxide.

By reaction with diazomethane in moist ether isopropylidene malonate is converted into a mixture of acetone and dimethyl malonate. A similar picture is observed in the case of cyclohexylidene malonate (III). It is quite probable that these reactions pass through the intermediate stage of cleavage of unstable enol ethers (IV) and (V), in as much as Meldrum's acid itself does not change on standing in moist ether. When moist ethereal diazomethane is replaced by a dry solution, an oily mixture can be obtained from Meldrum's acid, and spectrum data indicate that this contains the enol ether (IV).



(I), R = CH_3 (IV), R = CH_3

(III), R = (V), R = 

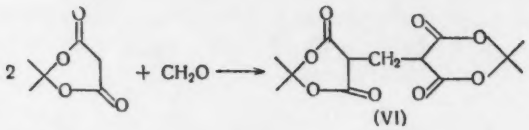
With piperidine Meldrum's acid and its cyclohexane analog (III) give well crystallizing nonhygroscopic salts, which decompose in boiling toluene with formation of a complex mixture of products which include 1-acetylpiperidine and the corresponding ketone (acetone or cyclohexanone).

Meldrum's acid has feeble nucleophilic properties and does not undergo cyanoethylation at room temperature (in aqueous dioxane with sodium carbonate as catalyst). Also, according to the literature [1], the silver salt of Meldrum's acid readily undergoes C-methylation under the action of methyl iodide, which contrasts with the behavior of the silver salt of 1,3-cyclohexanedione, which forms only the O-derivative [3]. In this property of the silver salt of Meldrum's acid the energetic unfavorability of its enol form is clearly manifest.

In its reaction with formaldehyde, isopropylidene malonate behaves like 1,3-cyclohexanedione [3]: under the action of formalin in presence of traces of piperidine there is ready formation of diisopropylidene methylenedimalonate (VI), whose structure was confirmed by hydrolytic cleavage to 1,1,3,3-propanetetracarboxylic acid.

Despite the presence of two β-dicarbonyl groupings, like 2,2'-methylenedi-1,3-cyclohexanedione, diisopropylidene methylenedimalonate titrates as a monobasic acid.

Alcohol	Alcohol + HCl	Alcohol	Alcohol + NaOH
VII	245 (8570)	230 (7210)	228 (6700)
		301 (5620)	301 (7100)
VIII	260 (6430)	257 (6470)	251 (15,100)
		315 (1490)	320 (12,200)

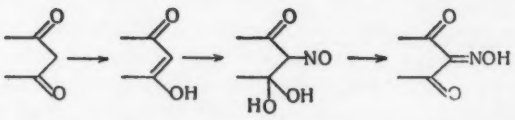


(VI)

$\xrightarrow[H_2O]{HCl}$ $(HCOC)_2CHCH_2CH(COOH)_2$

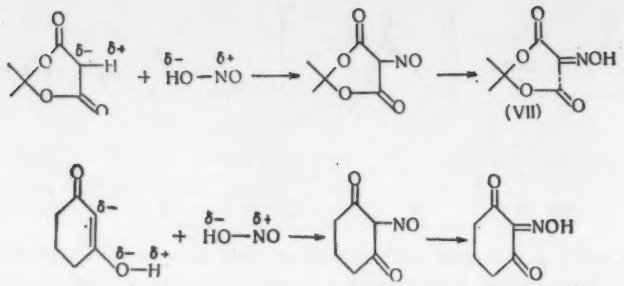
Under the action of nitrous acid in an aqueous medium Meldrum's acid undergoes nitrosation with formation of an almost colorless crystalline derivative, isopropylidene (hydroxyimino)malonate (VII). The oxime structure of the nitrosation product is confirmed by the resemblance of its ultraviolet spectra (characteristic change of the maxima with pH) to the spectra of 2-(hydroxyimino)dimethyl-1,3-cyclohexanedione (VIII) [4] (see table).

The fact that Meldrum's acid, which is unable to enolize in the undissociated state, reacts with nitrous acid in a strongly acid medium throws doubt on the generally accepted mechanism of the nitrosation of β-dicarbonyl compounds, which includes the stage of addition at the double bond of the enol form (Meyer and Lenhardt [5])



It must be mentioned that the only argument in favor of this scheme was the conversion of 3-ethoxycrotonic ester into 2-(hydroxyimino)acetoacetic ester under the action of nitrous acid in an aqueous medium. This experiment, however, cannot be regarded as convincing, for hydrolysis of the enol ether could precede nitrosation. Meyer and Lenhardt's scheme is contradicted also by the inability that we have found in the enol ethers of 1,3-cyclohexanedione and dimedon to undergo reaction with nitrous acid under the usual conditions (aqueous solution, 0 to + 5°).

It may be supposed on the basis of these results that, at least in some cases, the nitrosation of β-dicarbonyl compounds proceeds by the mechanism of electrophilic substitution with or without transfer of the reaction center.



Oxidation of isopropylidene and cyclohexylidene malonates with permanganate and with hydrogen peroxide in an alkaline medium is accompanied by cleavage of the ring with formation, respectively, of acetic and oxalic acids (together with acetone and cyclohexanone).

EXPERIMENT

Meldrum's acid (m.p. 94-95°) [1] and cyclohexylidene malonate (m.p. 95°) [6] were prepared by reaction of malonic acid with acetone and cyclohexanone, respectively, in acetic anhydride in presence of sulfuric acid.

Reaction of Meldrum's Acid with Diazomethane. A moist ethereal solution of diazomethane prepared from 7 g of 1-methyl-1-nitrosourea was gradually added to an ice-cooled suspension of 2.9 g of Meldrum's acid in 20 ml of ether. Reaction was very vigorous, and Meldrum's acid went rapidly (in the course of 10-15 minutes) into solution. After removal of ether and acetone by distillation we isolated 2.5 g (94%) of dimethyl malonate; b.p. 72-73° (14 mm); n_D^{20} 1.4140.

A dry ethereal solution of diazomethane prepared from 9 g of methylnitrosourea was added gradually to a suspension of 4.5 g of Meldrum's acid in 40 ml of dry ether at 0-5°. When the precipitate had dissolved, the mixture was evaporated to dryness at atmospheric pressure (60-70°), and the residue was vacuum-distilled. We obtained 2 g of oil; b.p. 65-70° (4 mm); n_D^{20} 1.4380; λ_{max} 257.5 mμ (log ε 3.161); infrared spectrum: 1743, 1802 cm^{-1} (C=O), 3002 cm^{-1} (CH at double bond).

Reaction of Meldrum's Acid with Piperidine. A solution of 1 g of piperidine in 10 ml of benzene was added to 1.5 g of Meldrum's acid in 10 ml of benzene. After 20 minutes there was a precipitate of 2.2 g (95%) of the piperidine salt, m.p. 115-116° (from benzene). Found N 6.12; 5.94%. $C_{11}H_{19}O_4N$. Calculated: N 6.11%. On treatment with 1:1 hydrochloric acid, the piperidine salt was converted completely into Meldrum's acid.

The piperidine salt of cyclohexylidenemalonic acid was prepared analogously; yield 94%; m.p. 114-115° (from benzene). Found: N 5.11; 5.02%. $C_{14}H_{24}O_4N$. Calculated: N 5.18%.

Thermal Decomposition of the Piperidine Salt of Meldrum's Acid. A mixture of 3.6 g of the piperidine salt of Meldrum's acid and 60 ml of toluene was boiled with a water separator until water ceased to separate (about 30 minutes). Acetone was detected in the aqueous distillate. From the toluene solution we isolated 2 g of 1-acetylpiperidine b.p. 68-70° (3 mm); n_D^{16} 1.4829. The hydrochloride had m.p. 93-94°, undepressed by admixture of a known sample.

On decomposition of the piperidine salt of cyclohexylidenemalonic acid under similar conditions we isolated cyclohexanone and 1-acetylpiperidine.

Reaction of Meldrum's Acid with Formaldehyde. A mixture of 1.5 g of Meldrum's acid, 1-2 drops of piperidine, and 10 ml of 10% formaldehyde was stirred for 90 minutes at room temperature. The precipitate formed was filtered off and dried in air. We obtained 1 g (66%) of diisopropylidene methylenedimalonate (VI), m.p. 156-157° (decomp.). Found: C 52.42; 52.32; H 5.23; 5.23%; titration equivalent 302, 304. $C_{13}H_{16}O_8$. Calculated: C 52.00; H 5.33%; titration equivalent 300.

Hydrolytic Cleavage of Diisopropylidene Methylenedimalonate. A mixture of 0.5 g of diisopropylidene methylenedimalonate and 10 ml of 1:1 hydrochloric acid was boiled for ten minutes and then vacuum-evaporated to dryness. We isolated 0.25 g (70%) of 1,1,3,3-propanetetracarboxylic acid, m.p. 164-166° (decomp.), undepressed by admixture with a known sample, which had m.p. 166-167° (decomp.) [7].

Reaction of Meldrum's Acid with Nitrous Acid. To a mixture of 6 g of Meldrum's acid, 6 g of sodium carbonate, and 2 g of sodium nitrite in 30 ml of water at from −5° to +5° gradual addition was made with stirring of 1:1 hydro-

chloric acid until the red color changed to yellow (acid reaction to Congo Red). After 20-30 minutes at from −5° to +5° the precipitate formed was filtered off and washed with ice water. We obtained 5.4 g (75%) of isopropylidene (hydroxyimino)malonate (VII), m.p. 107-109°. Recrystallization from benzene raised the melting point to 109-110°. The substance decomposed when kept for a long time (more than two days at about 20°). Found: C 41.49; 41.40; H 3.93; 4.13; N 8.21; 8.18%. $C_6H_7O_5N$. Calculated: C 41.62; H 4.05; N 8.10%.

Oxidation of Cyclohexylidene Malonate with Permanganate. To a mixture of 2.5 g of cyclohexylidene malonate and 2.5 g of sodium carbonate in 20 ml of water we added (20°) a 1% solution of permanganate until there was a permanent pink color. From the reaction mixture we isolated cyclohexanone and acetic acid.

Oxidation of Cylohexylidene Malonate with Hydrogen Peroxide. A mixture of 5 g of cyclohexylidene malonate, 5 g of sodium carbonate, and 40 ml of 15% hydrogen peroxide was kept for 12 hours at about 20°. We isolated 1.7 g of cyclohexanone and 1.5 g of oxalic acid.

The author is deeply grateful to T. M. Fadeeva for the spectrum investigations.

SUMMARY

Meldrum's acid reacts like 1,3-cyclohexanedione with nitrous acid and formaldehyde. Unlike 1,3-cyclohexanedione, Meldrum's acid does not form derivatives of the enol form under the action of moist ethereal diazomethane and of piperidine.

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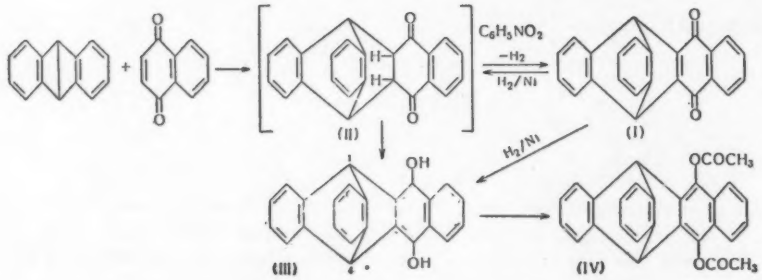
SYNTHESIS AND TRANSFORMATION OF (DIHYDROANTHRYLENE)-NAPHTHOHYDROQUINONE (CONTRIBUTION TO THE STEREOCHEMISTRY OF CATALYSIS)

A. A. Balandin, E. I. Klabunovskii, and L. V. Antik

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR
Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 12, pp. 2189-2192, December, 1961
Original article submitted July 6, 1961; additions made November 30, 1961

In previous investigations [1, 2] we studied the hydrogenation of dihydrotriptycenequinone [9, 10-dihydro-9,10-o-benzenoanthracene-1,4-dione] and bisdihydroanthrylenedihydrobenzoquinone [5,5a,7,12,13a,14-hexahydro-5,14: 7, 12-di-o-benzenopentacene-6,13-dione], which were prepared in accordance with [3]. It was of interest to extend the investigation to the hydrogenation of 5,12-dihydro-5,12-o-benzenonapthacene-6,11-dione (I), which is also a derivative of triptycene, but differs in the presence of a naphthoquinone grouping instead of dihydrobenzoquinone.

In the present work it was shown that (I) can be hydrogenated over a nickel catalyst under mild conditions. The reaction product is the hydroquinone 5,12-dihydro-5,12-o-benzenonaphthacene-6,11-diol (III). The hydrogenation of (I) into (III) occurs with or without passage through the form (II). The direct product of the diene synthesis is clearly the form (II).



It will be possible to reach some conclusion regarding the mechanism of this reaction when more experimental material has accumulated in this field.

The hydroquinone (III), which contains a naphthalene nucleus, is much less stable to oxidation than the corresponding hydroquinones in [1,2], in which there was a benzene nucleus in place of naphthalene. Such lower stability is in full accord with the annelation principle [4-7]. Actually, the hydroquinone (III) is very readily oxidized by atmospheric oxygen to the quinone (I) or to the corresponding quinhydrone. In spite of the fact that all operations in the isolation of the hydroquinone (III) were carried out in an atmosphere of nitrogen purified from traces of oxygen, we did not succeed in isolating (III) in a completely pure state. The hydroquinone (III) was characterized in the form of the quinhydrone, the diacetate, and the bis(phenylurethan).

An attempt to prepare the hydroquinone (III) by the condensation of anthracene and 1,4-naphthoquinone in an inert solvent (diethylbenzene) in an atmosphere of purified nitrogen at 140-150° for 24 hours showed that the (dihydroanthrylene)naphthohydroquinone formed in the course of the reaction was oxidized, probably by napthoquinone that had not yet reacted, to the quinone (I) and the corresponding quinhydrone, and we were unable to isolate it from the products of this reaction. Much of the anthracene remained unchanged. By further oxidation the quinhydrone was readily converted into the quinone (I).

This course of the reaction was confirmed in an attempt to prepare the diacetate (IV) by the condensation of anthracene and 1,4-naphthoquinone in acetic anhydride in an atmosphere of purified nitrogen. It was shown that under the given conditions the hydroquinone (III) formed is acetylated only partially and is for the main part oxidized to the quinone (I) by the naphthoquinone that had not yet reacted. Also, part of the 1,4-naphthoquinone was reduced to naphthalenediol, which was converted into the corresponding diacetate under the conditions of the reaction. Much of the anthracene remained unchanged. The structures of the diacetate (IV) and of the 1,4-naphthalenediol diacetate formed were checked by confirmatory syntheses.

EXPERIMENTAL

All operations with the hydroquinone (III) were carried out in an atmosphere of nitrogen purified from traces of oxygen by passage over incandescent reduced copper and through alkaline pyrogallol solution.

Quinone (I). This was prepared in accordance with [8, 9] by the diene synthesis; it was the monohydrate. Found: C 81.80; 81.95; H 4.66; 4.65%. $C_{24}H_{14}O_2 \cdot H_2O$. Calculated: C 81.80; H 4.57%. When it was dried in a vacuum for 2.5 hours at 130-135°, the water of crystallization was lost. Found: C 86.07; 85.84; H 4.37; 4.23%. $C_{24}H_{14}O_2$. Calculated: C 86.21; H 4.22%. The infrared spectrum of the quinone monohydrate contained a hydroxyl line, which was absent in the infrared spectrum of the anhydrous quinone (I).

Hydroquinone (III). This was prepared by the addition of one molecular proportion of hydrogen to the quinone (I) over Raney nickel in 1:1 alcohol-toluene at 45° at atmospheric pressure. The course of the hydrogenation is shown on the curve of the figure in the coordinates: rate of absorption of hydrogen [ml of H_2 (STP) per minute] and conversion (%). The first point on the curve corresponds to the first minute of the hydrogenation. The reaction was stopped after the absorption of one molecular proportion of hydrogen. The catalyzate was filtered and evaporated under reduced pressure in an atmosphere of pure nitrogen. The hydroquinone separated in colorless crystals, which rapidly oxidized in the air.

Quinhydrone of (III). This was obtained from a colorless solution of the hydroquinone (III) obtained by the hydrogenation of the quinone (I) by partial evaporation under reduced pressure in a stream of air. It formed black flat needles (from toluene; the recrystallization was carried out in an atmosphere of nitrogen); m.p. 267-268°. The melting point was determined in a sealed capillary in an atmosphere of nitrogen; when heated in an open capillary the black needles of the quinhydrone were converted at 267-268° into yellow prisms of (I), which melted at 280°. The quinhydrone firmly held one-half of a molecular proportion of water. Found: C 84.78; 84.74; H 4.60; 4.63%. $C_{24}H_{16}O_2 \cdot C_{24}H_{14}O_2 \cdot \frac{1}{2}H_2O$. Calculated: C 84.81; H 4.60%.

Diacetate (IV). The colorless solution of the hydroquinone (III) formed in the hydrogenation of 0.46 g of the quinone (I) was filtered from catalyst in an atmosphere of nitrogen and introduced into 100 ml of acetic anhydride. On removal of solvents (alcohol and toluene, in which the hydrogenation was carried out) the mixture was heated at a gentle boil for two hours. When cool, the solution was filtered, and the acetic anhydride was carefully decomposed with water. We isolated 0.55 g of almost colorless product (yield close to theoretical); colorless elongated rectangular plates (from glacial acetic acid); m.p. 284-286°. Found: C 81.01; 79.75; H 4.96; 5.04%. $C_{28}H_{20}O_4$. Calculated: C 79.98; H 4.795%.

Bis(phenylurethan) of (III). This was prepared by boiling the hydroquinone (III) in diethylbenzene solution in a nitrogen atmosphere for 2.5 hours with a large excess of phenyl isocyanate in presence of a very small amount of Na. The yield was about 70%. Spindle-shaped crystals (from toluene), m.p. 226-228°. Found: C 79.74; 79.67; H 4.76; 4.89%. $C_{38}H_{26}O_4N_4$. Calculated: C 79.43; H 4.66%.

Condensation of Anthracene with 1,4-Naphthoquinone in Acetic Anhydride. A mixture of 3 g of anthracene and 2.53 g of 1,4-naphthoquinone was heated at a gentle boil in 130 ml of acetic anhydride in an atmosphere of nitrogen for 15 hours. On cooling there was a precipitate of 2.85 g of a pale-yellow product, m.p. 193-205°. The mother solution was carefully diluted with water, when we isolated 0.03 g of a pale-pink product, m.p. 114-200°. Two sucessive recrystallizations of a small portion of the latter yielded a substance of m.p. 126-128°, undepressed by admixture of 1,4-naphthalenediol diacetate, which we prepared for this purpose by the hydrogenation of 1,4-naphthoquinone

over Raney nickel with subsequent acetylation of the resulting hydroquinone with acetic anhydride in a nitrogen atmosphere. A mixture of the two products (m.p. 193-205° and m.p. 114-200°), amounting to 0.68 g, taken in proportions in which they were isolated in the reaction were subjected to chromatographic separation. The mixture was dissolved in heptane and passed through a column of alumina. Elution was carried out at first with heptane, and then with a 1:2 mixture of benzene and heptane. From the first portion of the eluate we isolated 0.067 g of pure anthracene, from the second 0.06 g of a mixture of anthracene and the quinone (I), and from the third 0.292 g of the quinone (I), m.p. 278-280°, undepressed by admixture of pure (I). The remaining product was eluted with acetone. On removal of acetone we obtained 0.191 g of a pale-brown residue. On washing this with hot octane we isolated a product soluble in octane and of m.p. 80-100°; it appeared to be contaminated 1,4-naphthalenediol diacetate.

The octane-insoluble product was precipitated by water from its solution in glacial acetic acid; it then had m.p. 279-282°, undepressed by admixture of the diacetate (IV).

The authors thank B. V. Lopatin for the determination of infrared spectra.

SUMMARY

1. As a result of the hydrogenation of the quinone (I) over Raney nickel there was formed a previously undescribed readily oxidizable hydroquinone (III), which was characterized as the quinhydrone, the diacetic ester, and the bis(phenylurethan).

2. In the condensation of anthracene with 1,4-naphthoquinone in acetic anhydride, the formation of the diacetate (IV) is accompanied by oxidation of the hydroquinone (III) to the quinone (I) by unchanged 1,4-naphthoquinone. Under the conditions of the reaction the latter gives 1,4-naphthalenediol diacetate.

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ALKYLATION OF PHENOLS WITH BIFUNCTIONAL COMPOUNDS

COMMUNICATION 5. CATALYTIC ALKYLATION OF m- AND p-CRESOLS WITH 1,3-BUTANEDIOL

N. I. Shuikin, E. A. Viktorova, and I. E. Pokrovskaya

M. V. Lomonosov Moscow State University

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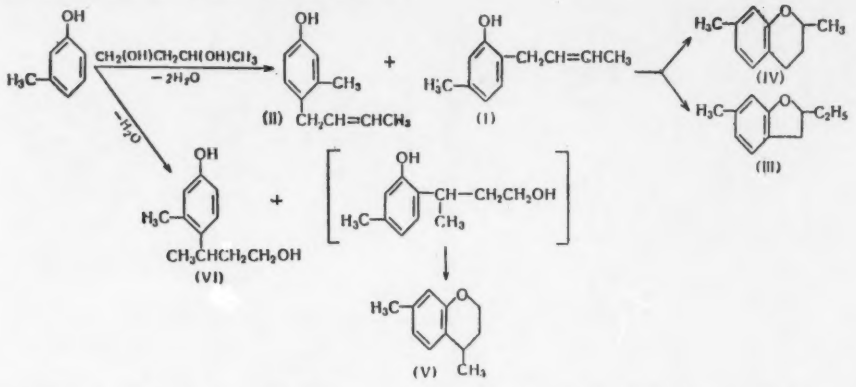
In continuation of our work on the alkylation of phenols with bifunctional compounds [1-4] we investigated the alkylation of m- and p-cresols with 1,3-butanediol. This compound was used by Tsukervanik [5] and by Losev [6] for the alkylation of aromatic hydrocarbons [5] and phenol [6]. The main product of the alkylation of benzene with 1,3-butanediol was found to be 3-phenyl-1-butanol, so that reaction went exclusively at the secondary hydroxyl. Losev [6] was unable to isolate any individual products in the alkylation of phenol with 1,3-butanediol.

We carried out the alkylation of m-cresol with 1,3-butanediol at 150° and 250° in presence of zinc chloride deposited on alumina. It was found that at 150° scarcely any reaction occurred, but at 250° the yield of alkylation products attained 74%. Of the alkylation products, as well as a small amount (5.7%) of 3-(4-hydroxy-2-methylphenyl)-1-butanol, we isolated some substances that we obtained previously in the alkylation of m-cresol with 3-buten-1-ol [3] and with butadiene: 4-(2-butenyl)-3-methylphenol, 2-(2-butenyl)-5-methylphenol, and its cyclization products 2-ethyl-6-methylcoumaran and 2,7-dimethylchroman, which leads one to suppose that in the main the reaction proceeds through the intermediate formation of butadiene.



For p-cresol under identical conditions the yield of alkylation products was 69%, and we isolated analogous substances. From the catalyzate obtained in the alkylation of p-cresol in presence of phosphoric acid we isolated the same substances with the exception of 4,6-dimethylchroman. In all experiments a considerable amount of high-boiling substances was formed. Thus, under our reaction conditions alkylation at the secondary alcohol group was preceded by dehydration and formation of butadiene from 1,3-butanediol; the butadiene then alkylated the cresol. To a slight extent there was also alkylation at the secondary alcohol group. As regards the 2-ethyl-6-methylcoumaran and 2,7-dimethylchroman found in the catalyzates, they were undoubtedly formed by the cyclization of 2-(2-butenyl)-5-methylphenol, and 4,7-dimethylchroman was probably the product of the cyclization of the intermediately formed 3-(2-hydroxy-4-methylphenyl)-1-butanol.

EXPERIMENTAL

The alkylation of m- and p-cresols with 1,3-butanediol in presence of zinc chloride (20% on alumina) was carried out in shaking autoclaves under the vapor pressure of the system (1-2 atm). The shaking autoclaves had working volumes of 150 ml; they were mounted in electric furnaces, the temperature of which was controlled by an ERM-47 thermoregulator.

TABLE 1. Results of the Alkylation of m-Cresol with 1,3-Butanediol at 250° in Presence of H_3PO_4

Molar ratio of reactants (cresol : 1,3-butanediol)	Amt. of catalyzate (% on reactants taken)	Total yield of individual products (%)	Yields of alkylation products (%)							
			2-(2-butenyl)-6-methylphenol	4-(2-butenyl)-3-methylcoumaran	2-ethyl-6-methylcoumaran	2,7-dimethylchroman	4,7-dimethylchroman	3-(4-hydroxy-2-methylphenyl	3-bis(4-hydroxy-2-methylphenyl)butane	high-boiling and polymeric substances
1 : 1	30	48.8	10.7	9.0	4.4	8.8	1.8	5.0	4.1	24.1
2 : 1	30	74.0	33.5	7.3	6.9	11.1	5.7	4.8	4.7	21.7
1 : 1	15	51.6	17.4	11.0	2.8	9.7	1.6	7.5	2.6	24.7

TABLE 2. Results of the Alkylation of p-Cresol with 1,3-Butanediol

Catalyst	Molar ratio of reactants (p-cresol: 1,3-butanediol)	Amt. of catalyzate (% on reactants taken)	Temp. of expt. (°C)	Total yield of individual reaction products (%)	Yields of alkylation products (%)				
					2-ethyl-5-methylcoumaran	2,6-dimethylchroman	4,6-dimethylchroman	2-(2-butenyl)-4-methylphenol	high-boiling and polymeric products
H_3PO_4	1:1	200	200	42.8	30.1	7.4	–	5.3	25.0
Ditto	2:1	200	200	53.0	38.0	11.3	–	3.7	35.3
$ZnCl_2 + Al_2O_3$	1:1	30	250	38.3	20.1	10.9	8.0	2.2	18.5
The same	1:1	30	300	35.0	3.2	21.8	10.1	–	32.0
" "	2:1	30	250	69.2	33.4	15.5	14.3	5.0	14.8
" "	1:1	15	250	49.4	24.0	13.0	8.4	4.0	22.2

The alkylation of p-cresol with 1,3-butanediol was also carried out in presence of phosphoric acid (sp. gr. 1.74) in a round-bottomed flask fitted with mechanical stirrer, reflux condenser, and dropping funnel. After the separation of the catalyzate from the catalyst, the reaction product was dissolved in ether, and the ethereal solution was treated twice with sodium hydroxide: first with a 10% solution, and then with a 30% solution. The alkaline extracts were acidified with hydrochloric acid, with cooling, until there was a positive test with Congo Red paper. The phenols liberated were extracted with ether, and the ether extract was washed with water and dried with calcium chloride. Ether was then distilled off, and the neutral reaction products were vacuum-fractionated. The results of experiments on the alkylation of m- and p-cresols are given in Tables 1 and 2.

The substances that we isolated from the products of the alkylation of m- and p-cresols with 1,3-butanediol had the following properties.

Products of the alkylation of m-cresol. I. 2-(2-Butenyl)-5-methyl-phenol [3,7]: b.p. 109-111° (5 mm); n_D^{20} 1.5382; d_4^{20} 1.0069. II. 4-(2-Butenyl)-3-methylphenol [3]; b.p. 115-117° (5 mm); n_D^{20} 1.5393; d_4^{20} 0.9986; m.p. of hydroxyacetic acid derivative, 109-110° [3]. The number of mobile hydrogen atoms in this phenol, as determined by Terent'ev's micro method [8], was two. III. 2-Ethyl-6-methylcoumaran [3]; b.p. 91-92° (5 mm); n_D^{20} 1.5252; d_4^{20} 0.9922. IV. 2,7-Dimethylchroman [3]; b.p. 100-102° (5 mm); n_D^{20} 1.5290; d_4^{20} 0.9980. V. 4,7-Dimethylchroman; b.p. 110-111° (5 mm); n_D^{20} 1.5282; d_4^{20} 0.9951. VI. 3-(4-hydroxy-2-methylphenyl)-1-butanol; b.p. 136-140° (4-5 mm); n_D^{20} 1.5460; d_4^{20} 1.0221; m.p. of hydroxyacetic acid derivative, 98-99°.

Products of the alkylation of p-cresol. I. 2-(2-Butenyl)-4-methylphenol [3, 7]; b.p. 112-114° (9 mm); n_D^{20} 1.5338; d_4^{20} 0.9998; m.p. of hydroxyacetic acid derivative, 106-108° [3, 7]. II. 2-Ethyl-5-methylcoumaran [3, 7]; b.p. 93-95° (5 mm); n_D^{20} 1.5232; d_4^{20} 0.9950; III. 2,6-Dimethylchroman; b.p. 99-101° (5 mm); n_D^{20} 1.5282; d_4^{20} 0.9976. IV. 4,6-Dimethylchroman; b.p. 115-118° (6 mm); n_D^{20} 1.5288; d_4^{20} 0.9964.

SUMMARY

1. An investigation was made of the alkylation of m- and p-cresols with 1,3-butanediol in presence of zinc chloride (20% on alumina) or phosphoric acid.

2. The products of the alkylation of m- and p-cresols with 1,3-butanediol were mainly the isomeric butenylcresols and products of their cyclization, identical with the corresponding products of the alkylation of cresols with 3-buten-1-ol.

3. The total yields of individual products in the alkylation of m- and p-cresols at 250° in presence of $ZnCl_2$ on alumina were 74.0% and 69.2% respectively. In all cases 14.8-35.3% of polymeric substances was formed; the compositions and structures of these have not yet been established.

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THERMAL ALKYLATION OF TETRAHYDRO-2-METHYLFURAN WITH ETHYLENE

N. I. Shuikin and B. L. Lebedev

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR
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We recently showed that tetrahydrofuran can be thermally alkylated with ethylene [1]. It was of interest in this connection to determine the effect of the presence of a methyl group at the position at which ethylene enters the tetrahydrofuran ring. With this object we investigated the reaction between tetrahydro-2-methylfuran and ethylene under various conditions (variation of temperature, reaction time, and proportions of reactants). We showed that in the reaction of tetrahydro-2-methylfuran with ethylene in the range 325-375° two main reactions were observed: the alkylation and the isomerization of the tetrahydro-2-methylfuran. It was found that ethylene attacks the tetrahydrofuran ring in the 5-position. Earlier, one of us in collaboration with Bel'skii [2] discovered the isomerization of the tetrahydrofuran ring at 250° over platinized charcoal with formation of aliphatic ketones. In the present work we showed that similar isomerization of tetrahydro-2-methylfuran occurs at 325-375° in absence of catalysts. The alkylation of tetrahydro-2-methylfuran was carried out by the procedure that we described previously [1]. In all experiments we took 0.75 mole of tetrahydro-2-methylfuran for reaction. The reaction products were analyzed by the methods of gas-liquid chromatography and infrared spectroscopy [3, 4]. Fractionation of the products of the alkylation of tetrahydro-2-methylfuran with ethylene through a column of 40-plate efficiency gave ethyltetrahydromethylfuran of b.p. 117.5-118°; n_D^{20} 1.4168; d_4^{20} 0.8440. Measurements of the intensities of the absorption bands of the C−H valence vibrations of the CH_3 and CH_2 groups (at 2965 and 2926 cm^{-1}) showed that the substance isolated had two CH_3 groups and three CH_2 groups and was indeed ethyltetrahydromethylfuran. Found: C 73.33; 73.20; H 12.43; 12.44%. $C_7H_{14}O$. Calculated: C 73.62; H 12.36%.

On investigation of the composition of the alkylation products in the combined catalyzate from all experiments were found 2-pentanone; b.p. 99-100°; n_D^{20} 1.3910; d_4^{20} 0.8130. A special experiment showed that at 350° in

Effect of Pressure on the Rate and Course of the Reaction at 350°

Duration of expt. (min)	Pressure (atm)		Amt of catalyzate (g)	Amt. of tetrahydromethylfuran that acts		Yield of 2-pentanone		Yield of ethyltetrahydromethylfuran			Yield of polyalkyl product
	ethylene	nitrogen		%	% in catalyzate	% of theor.	% in catalyzate	% on amt. taken	% on amt. that reacts	% in catalyzate	% in catalyzate
90	50	–	69.9	17.8	16.5	4	3.7	2.1	11.8	2.6	19.6
90	10	40	63.4	17.4	16.4	5.4	5.5	1	6	1.4	8.0
90	–	50	62.4	83	85.9	13.6	14.1	–	–	–	–

presence of nitrogen at 50 atm the isomerization of tetrahydro-2-methylfuran into 2-pentanone did indeed occur (table). This is confirmed by spectroscopic analysis. The spectrum of the fraction of b.p. 98-104° was determined in the range 1600-1800 cm^{-1}. It contained C=O absorption bands at 1715 cm^{-1} (strong) and 1735 cm^{-1} (weak). The

first is due to the C=O valence vibrations in a ketone group, and the second to these vibrations in an aldehyde group [5]. Comparison of the 2-pentanone isolated with the standard by chromatographic analysis gave satisfactory results.

The establishment of the fact of the thermal isomerization of tetrahydro-2-methylfuran into 2-pentanone under our conditions considerably facilitates the resolution of the question of the possible place of the introduction of the ethylene into the tetrahydromethylfuran molecule. It would appear that the alkylation of the CH_3 group and of the tetrahydrofuran ring in the 2-position cannot occur, for the 2-ethyltetrahydro-2-methylfuran which would then be formed has two CH_3 and four CH_2 groups, and tetrahydropropylfuran has one CH_3 and five CH_2 groups, which is not in accord with the results obtained.

There is no information in the literature on the physical properties of 3-ethyltetrahydro-2-methylfuran and 4-ethyltetrahydro-2-methylfuran, but it is known that the ketones and aldehydes formed by their isomerization have b.p. about 140°. The isomerization of 2-ethyltetrahydro-5-methylfuran gives 2- and 3-heptanones, b.p. 147-150°. By fractionation through a column, from the combined catalyzate we isolated a ketone of b.p. 147.5-149°, n_D^{20} 1.4143; and d_4^{20} 0.8205, with a semicarbazone of m.p. 104.5-105.5°, which corresponds to the melting point of the semicarbazone of 3-heptanone.

Hence, at 325-375° and 10-50 atm of ethylene, the tetrahydromethylfuran ring is alkylated in the 5-position with formation of 2-ethyltetrahydro-5-methylfuran. This probably indicates the enhanced reactivity of the α-hydrogen atoms. In the isomerization of tetrahydro-2-methylfuran ring opening occurs at the C–O bond most remote from the methyl group, whereas the isomerization of the 2-ethyltetrahydro-5-methylfuran formed occurs with ring opening mainly at the C–O bond adjacent to the methyl group.

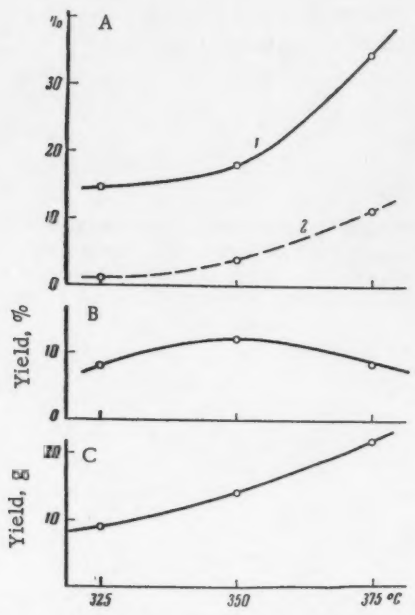

Fig. 1. Effect of temperature on A) the conversion of tetrahydro-2-methylfuran (1) and the extent of the isomerization of tetrahydro-2-methylfuran (2); B) the yield of 2-ethyltetrahydro-5-methylfuran; C) the yield of polyalkylated products.

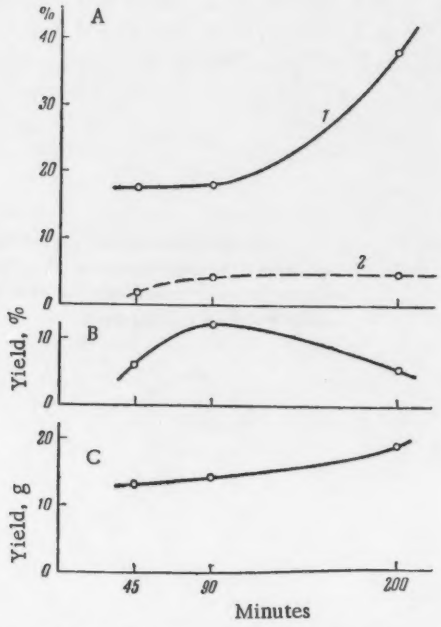

Fig. 2. Effect of reaction time on A) the conversion of tetrahydro-2-methylfuran (1) and the extent of the isomerization of tetrahydro-2-methylfuran (2); B) the yield of 2-ethyltetrahydro-5-methylfuran; C) the yield of polyalkylated products.

We studied the effect of temperature, reaction time, and proportions of reactants on the conversion of tetrahydro-2-methylfuran, its isomerization, and the yield of alkylation products.

Figure 1 shows the results of investigations to determine the effect of temperature at a reaction time of 90 minutes and an ethylene pressure of 50 atm. With rise in temperature the amount of unchanged tetrahydro-2-methyl-

furan rose sharply. The best yield (11.8%) of ethyltetrahydromethylfuran was obtained at 350°. The yield of polyalkylated product was almost proportional to the rise in temperature. With rise in temperature the extent of the isomerization of tetrahydro-2-methylfuran into 2-pentanone rose to 11.6%. The effect of the reaction time at 350° is shown in Fig. 2. With increase in reaction time to 200 minutes the amount of tetrahydro-2-methylfuran that reacts increased to 37.7%. The extent of isomerization was almost the same for reaction times of 90 and 200 minutes. The maximum yield of ethyltetrahydromethylfuran was obtained at a reaction time of 90 minutes. The yield of polyalkylated product was almost proportional to the increase in reaction time.

As regards the proportions of the reactants, with increase in the amount of ethylene by change in pressure from 10 to 50 atm (see table) the yield of ethyltetrahydromethylfuran was doubled and that of the polyalkylated products almost tripled. It is interesting that with increase in the amount of ethylene taken in the reaction the extent of the isomerization of tetrahydro-2-methylfuran into 2-pentanone fell, as will be seen from the table.

SUMMARY

1. In the temperature range 325-375° under a pressure of ethylene of 10-50 atm there occurs the thermal alkylation of the ring of tetrahydro-2-methylfuran in the 5-position with formation of 2-ethyltetrahydro-5-methylfuran.

2. Under these conditions there is simultaneous partial isomerization of the tetrahydro-2-methylfuran into 2-pentanone.

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CATALYTIC SYNTHESIS OF HIGH-DENSITY $C_{20}-C_{38}$ ISOPARAFFINS

A. P. Meshcheryakov, E. I. Erzyutova, and Go Chun'-i

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR

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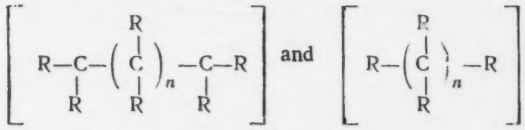
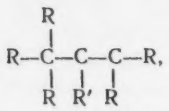
There are at present very few data on high-density (about 0.85 and higher) $C_{16}-C_{38}$ isoparaffins. However, calculation shows that it is possible for isoparaffins to exist with a density even approaching unity. One of us [1] calculated the densities of more than 100 $C_{12}-C_{36}$ isoparaffins that have not yet been described and listed some of these of maximum density: values of d_4^{20} – $C_{12}H_{26}$, 0.8246; $C_{13}H_{28}$, 0.8420; $C_{14}H_{30}$ – 0.8576; $C_{15}H_{32}$ – 0.8718; $C_{16}H_{34}$ – 0.8844; $C_{24}H_{50}$ – 0.98; $C_{28}H_{58}$ – 0.99; $C_{36}H_{74}$ – 1.00.

From the results of the calculation it follows that the highest densities are possessed by isoparaffins of the type



i.e., those with several adjacent quaternary carbon atoms in the middle of the paraffin chain. The dispersion of the quaternary and tertiary carbon atoms along the chain of the paraffin molecule appreciably reduces the density.

With the object of preparing isoparaffins of high density we brought about the catalytic dimerization of some trisubstituted ethylene derivatives, namely $C_{10}-C_{19}$ alkenes, and by the hydrogenation of their dimers we obtained $C_{20}-C_{38}$ isoparaffins of the type



in which R = $-C_3H_7$, $-C_4H_9$, $-C_5H_{11}$, n-C_6H_{13}; R' = ethyl, propyl, butyl, pentyl. We first calculated the densities of the isoparaffins which we planned to synthesize by the use of Tatevskii's method [2] with $A_{2,2} = 16.3$ [1] It should be noted that the value of $A_{2,2} = 16.3$ is very close also to $A_{2,2} = 16.27$ for the alkyl chain of 2-alkyl-1,1-dimethylcyclopropanes [3]. The calculations showed that the densities of these isoparaffins should be about 0.84 and higher. Recently, Levina and co-workers [4] have prepared $C_{15}-C_{17}$ isoparaffins of density 0.8268-0.8464.

The original monomers-trisubstituted ethylene derivatives-were prepared by the dehydration of the corresponding tertiary alcohols. We prepared 4-propyl-3-heptene, 5-butyl-4-nonene, 5-propyl-5-nonene, 5-butyl-5-decene, and 7-heptyl-6-tridecene; their constants are given in Table 1.

In the Raman spectra of these olefins there is a very intense line in the region of 1660 cm^{-1} and frequencies in the regions of 3000 and 3080 cm^{-1} are absent, which indicates a nonterminal position of the double bond in these olefins. By way of example we give the spectrum of 7-hexyl-7-tridecene: $\Delta\nu$ (cm^{-1}): 514(1), 818(1), 845(2b), 866(3b), 894(4b), 955(3b), 1000(2b), 1020(3b), 1074(4b), 1140(5b), 1131(1b), 1192(2), 1300(6b), 1338 (2), 1378 (1b), 1440 (10b), 1458(10b), 1660(10), 2850(10b, db), 2895 (10b), 2834 (8 sp), 2963 (8).

The olefins were dimerized under the influence of concentrated sulfuric acid in accordance with the scheme:

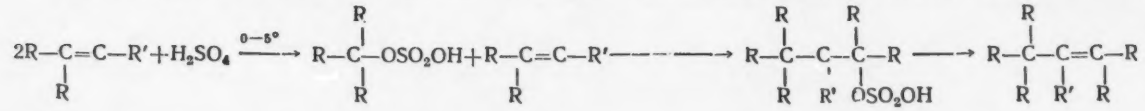
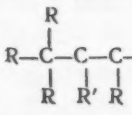
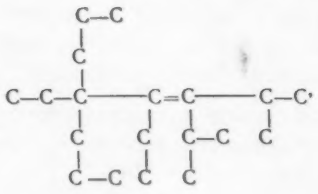


TABLE 1. Properties of Original Monomers

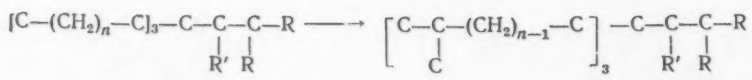
Original alcohol	Monomer (olefin) obtained	B.p. in °C (p in mm)	d_4^{20}	$n^{20}D$	ν^{20} (centistoke)	F.p. (°C)	Found (%)		Calculated (%)	
							C	H	C	H
Tripropylmethanol	$C_{10}H_{20}$ 4-propyl-3-heptene	161–163	0.7502	1.4922		<–70				
Dibutylpropylmethanol	$C_{12}H_{24}$ 5-propyl-5-nonene	65–67(4–5)	0.7696	1.4365	1.5	<–70	86.65	14.55	85.63	14.3
Tributylmethanol	$C_{13}H_{26}$ 5-butyl-4-nonene	91–92(9); 213–214(760)	0.7757	1.4390	2.15	<–70	85.68	14.29		
Dibutylpentylmethanol	$C_{14}H_{28}$ 5-butyl-5-decene	105(7–8)	0.7781	1.4415	2.76	<–70	85.50	14.49		
Trihexylmethanol	$C_{19}H_{38}$ 7-hexyl-6-tridecene	168–170(10)	0.7991	1.4492	6.21	<–65	85.71	14.00	85.63	14.37

As a result of the dimerization of the olefins we obtained five dimers (Table 2), which were hydrogenated into isoparaffins of composition C_{20}–C_{38} and of type  , i.e., containing a quaternary carbon and two tertiary carbons in adjacent positions. The dimer prepared from 4-propyl-3-heptene, i.e., 5-ethyl-4,6,6-tripropyl-4-nonene, was ozonized. In the analysis of the ozonization products we isolated a ketone, the semicarbazone of which had m.p. 136-137° (the m.p. of the semicarbazone of dipropyl ketone is 132° [5], and the corresponding values for isopropyl propyl ketone and diisopropyl ketone are 119° [6] and 153° [7]). The somewhat high melting point of the semicarbazone indicates that in the ozonolysis product of the dimer, apart from dipropyl ketone, there was also a little diisopyl ketone. It follows that in the dimerization of 4-propyl-3-heptene partial isomerization occurred and, together with the main dimer, i.e. 5-ethyl-4, 6,6-tripropyl-4-nonene, a still more highly branched dimer of the type



was formed, and this gave diisopropyl ketone on ozonization.

As will be seen from Table 3, the isoparaffins that we prepared have densities that are somewhat lower than the values calculated by Tateevskii's method [2]. Thus, the density of the isoparaffin $C_{38}H_{78}$ that we prepared (see Table 3) is 0.8498, whereas the calculated value is 0.8518. It is possible that the density of the isoparaffin was lower because of the formation of structures containing more methyl groups, i.e., because of the isomerization of groups of normal structure



Such isomerization of alkyl groups, e.g., in 7,7,9-trihexyl-8-pentylpentadecane (d_4^{20} 0.8518) would lead to the formation of an isomer of somewhat lower density (calculated 0.8510).

TABLE 2. Properties of Dimers (Isoolefins) Obtained

Original monomer	Dimer (isoolefin)	B.p. in °C (P in mm)	d_4^{20}	n_D^{20}	ν^{20} (centistoke)	F.p. (°C)	Found %		Calculated %	
							C	H	C	H
4-propyl-3-heptene	5-Ethyl-4,6,6-tripropyl-4-nonene $C_{20}H_{40}$	150–155 (9)	0.8420	1.4660	23.13	−58	86.14	13.99	85.63	14.37
5-propyl-5-nonene	7-Butyl-5,6,7-tripropyl-5-undecene $C_{24}H_{48}$	189–192 (4–5)	0.8401	1.4660	44.41	−50	85.56	14.12	85.63	14.37
5-butyl-4-nonene	5,5,7-Tributyl-6-propyl-7-undecene $C_{26}H_{52}$	205–208 (10–11)	0.8449	1.4672	78.57	−40	85.62	14.10	85.63	14.37
5-butyl-5-decene	5,6,7,7-Tetrabutyl-5-dodecene $C_{28}H_{56}$	202–205 (8–9)	0.8422	1.4670	102.8	−40	85.60	14.31	85.63	14.37
7-hexyl-6-tridecene	7,7,9-Trihexyl-8-pentyl-8-pentadecene $C_{38}H_{76}$	260 (5–6)	0.8512	1.4714	239	−35	85.51	14.16	85.63	14.37

TABLE 3. Properties of Hydrogenated Dimers (C_{20}–C_{38} Isoparaffins)

Hydrogenated dimer (isoparaffin)	Molecular weight		B.p. in °C (p in mm)	Density d_4^{20}		n_D^{20}	ν^{20} (centistoke)	F.p. (°C)	Found %		Calculated %	
	found	calculated		found	calculated				C	H	C	H
5-Ethyl-4,5,5-tripropylnonane $C_{20}H_{42}$	280.01	282.54	160–161(7) 328(760)	0.8438	0.8443	1.4630	29.6	−40	85.3	14.72	85.01	14.98
7-Butyl-5,6,7-tripropylundecane $C_{24}H_{50}$	330.8	338.64	182–189 (7–8) 345 (760)	0.8412	0.8470	1.4626	61.94	−43	85.40	14.72	85.11	14.88
5,5,7-Tributyl-6-propylundecane $C_{26}H_{54}$	361.1	366.69	186–187 (5–6) 354 (760)	0.8446	0.8480	1.4640	113.7	−38	85.9	14.02	85.16	14.84
5,6,7,7-Tetrabutyldodecane $C_{28}H_{58}$	388.91	394.74	227–228 (7–8) 390 (760)	0.8432	0.8488	1.4644	130	−38	85.64	14.35	85.19	14.81
7,7,9-Trihexyl-8-pentylpentadecane $C_{38}H_{78}$	525	535	266 (5) 412 (760)	0.8498	0.8518	1.4678	341	−35	85.47	14.59	85.17	14.69 14.69

To elucidate some of the structural peculiarities of the paraffins synthesized we investigated their infrared spectra in the 3-4 μ region and determined the numbers of methylene and methyl groups from the intensities of the bands for these groups [8] in accordance with the method developed by Egorov and Shlyapochnikov [9]. The results are summarized in the figure, in which we give the straight line characteristic for n-alkanes and two straight lines for the hydrogenated monomers of T-form structure ($C_{10}-C_{19}$)* and for their dimers ($C_{20}-C_{38}$). As the figure shows, the straight lines are parallel. This indicates that in all the hydrocarbons investigated the number of methylene groups increases proportionally with the increase in molecular weight and is in accord with the structure proposed. The contribution to the intensity made by the CH_2 groups of the hydrogenated dimers was found to be less than the amount calculated, and the contribution of the CH_3 groups was greater. From this we may conclude that there is partial isomerization of the n-alkyl groups in the isoparaffins in the process of the dimerization of the monomers. As stated above, this is confirmed by the isolation of dipropyl ketone with admixture of diisopropyl ketone from the products of the ozonolysis of 5-ethyl-4,6,6-tripropyl-4-nonene.

Comparison of the properties of the paraffins obtained (see Table 3) shows that the catalytic dimerization of olefins with subsequent hydrogenation provides a method for the preparation of paraffins without any profound isomerization of the monomers or dimers and such that the calculated densities of the paraffins are close to the values found experimentally.

EXPERIMENTAL

The monomers (trisubstituted ethylene derivatives) were prepared by the dehydration of tertiary alcohols, which were synthesized by the Grignard reaction by the reaction of the corresponding esters with the alkylmagnesium halide.

We prepared: 1) Tripropylmethanol ($C_{10}H_{22}O$); yield 66%; b.p. 193–195°; d_4^{20} 0.8340; n_D^{20} 1.4340. The literature [10] gives: b.p. 193–195°; d_4^{20} 0.8338, n_D^{20} 1.4355. 2) Dibutylpropylmethanol ($C_{12}H_{24}O$); yield 54%; b.p. 112–114° (15 mm); d_4^{20} 0.8399; n_D^{20} 1.4420. The literature [11] gives: b.p. 113.6–114.2° (15 mm); d_4^{20} 0.8370; n_D^{20} 1.4419. 3) Tributylmethanol ($C_{13}H_{26}O$); yield 77%; b.p. 124–125° (12 mm); d_4^{20} 0.8442; n_D^{20} 1.4440. The literature [12] gives: b.p. 120° (10 mm); d_4^{20} 0.8440; n_D^{20} 1.4448. 4) Dibutylpentylmethanol ($C_{14}H_{28}O$); yield 70%; b.p. 139–141° (15 mm); d_4^{20} 0.8454; n_D^{20} 1.4420. The literature [13] gives: b.p. 90–92° (2 mm); d_4^{20} 0.8345; n_D^{20} 1.4450. 5) Trihexylmethanol; yield 66%; b.p. 150–153° (4–5 mm); d_4^{20} 0.8408; n_D^{20} 1.4492. The literature [14] gives: b.p. 153–154° (4–5 mm); d_4^{20} 0.8365; n_D^{20} 1.4496.

The alcohols were dehydrated by Ziegler's method [15] by heating them in glacial acetic acid solution with a few drops of concentrated sulfuric acid in a water bath for 20-30 minutes. The resulting isoolefins were washed with water, with saturated potassium carbonate solution, and again with water; they were dried over calcium chloride, and repeatedly distilled over sodium through a column of 18-plate efficiency. The properties of the monomers obtained are given in Table 1.

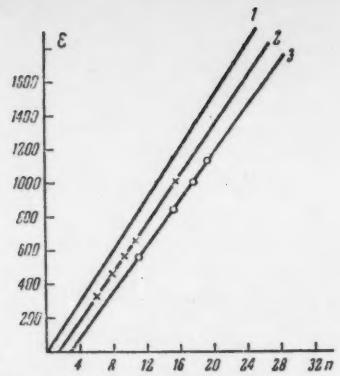
These constants are in good accord with values given in the literature [14, 16-19]. All the monomers that we prepared were hydrogenated in an autoclave over Bag's catalyst at 180-200°.

$C_{20}-C_{38}$ isoolefins were prepared by the dimerization of trisubstituted ethylene derivatives in presence of 100% sulfuric acid. The dimerization was carried out at 0-2°. The amount of acid taken was 10% by volume, and this was added dropwise with stirring over a period of two hours. The reaction mixture was then stirred further at 0-2° for six hours. The resulting dimer was separated from the alkyl hydrogen sulfate and was washed with water, with 10% sodium solution, and again with water; it was dried and repeatedly vacuum-distilled over sodium through a column of 18-plate efficiency. The properties of the isoolefins obtained are given in Table 2.

In the fractionation of the dimers we isolated also some hydrogenated monomers. It is evident that in the course of the dimerization there occurred some disproportionation, and part of the original olefin was hydrogenated to the paraffin.

To prove the structure of the isoolefins obtained, one of them, namely 5-ethyl-4,6,6-tripropyl-4-nonene ($C_{20}H_{40}$) was ozonized. The ozonization was carried out in dry chloroform solution in an ozonizator producing 0.48 g of ozone per hour. The ozonides were decomposed first with water (at 20°), and then with hydrogen peroxide with stirring and heating in a water bath. In the ozonization of 5-ethyl-4,6,6-tripropyl-4-nonene we isolated dipropyl ketone containing a little diisopropyl ketone. Its semicarbazone melted at 136-137°. To determine the mixture melting point we specially synthesized dipropyl ketone. The semicarbazone prepared from this melted at 132-133°, and the melting

*For each CH_2 group of the T-form structure there are, on the average, 75 units of intensity.



Infrared spectra of hydrocarbons investigated: 1) n-alkanes; 2) T-shaped paraffins; 3) olefin dimers (n = number of carbon atoms).

point in the mixture test was 134-135°. In the ozonization we isolated also a high-boiling ketone, but did not succeed in preparing derivatives of this.

All the isoolefins that we obtained were hydrogenated under pressure in an autoclave over Bag's catalyst at 180–200°.

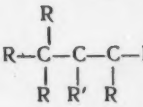
The properties of the hydrogenated dimers are given in Table 3.

SUMMARY

1. A study was made of the catalytic dimerization of five olefins, namely C_{10}–C_{19} trisubstituted ethylene derivatives, and the products of the hydrogenation of these dimers were prepared.

2. In the course of the dimerization partial isomerization of the dimers occurred.

3. The calculated densities of the resulting C_{20}–C_{38} isoparaffins of type



(in which R = propyl, butyl, pentyl, hexyl) are extremely close to the experimentally found values. Increase in the length of the side group in isoparaffins of this type from 3 to 6 carbon atoms has no substantial effect on the change in their density and freezing point.

4. With increase in the molecular weight of the isoparaffins obtained there is a sharp increase in their viscosity.

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ACCELERATION AND RETARDATION OF THE CRACKING OF HYDROCARBONS IN VARIOUS MEDIA

Ya. M. Paushkin, A. V. Topchiev, A. V. Nepryakhina,

P. G. Anan'ev, and N. N. Dmitrevskii

Institute of Petrochemical Synthesis, Academy of Sciences, USSR
Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk,
No. 12, pp. 2204-2209, December, 1961
Original article submitted May 9, 1961

The generally accepted mechanism of the thermal decomposition of hydrocarbons is the chain free-radical mechanism proposed by Rice [1-3]. In studies of the thermal transformations of the thermal transformation of hydrocarbons, Frost, Dintsev, Stepukhovich, and others [4-12] found that the rate of the decomposition of paraffins falls with increase in the extent of the decomposition, i.e., there is self-inhibition of thermal decomposition, and the part of inhibitors is played by the olefins (ethylene, propene, isobutene, etc.) formed in the process. It was shown in subsequent investigations [13, 14] that, other conditions being equal, isobutene retards the decomposition of hydrocarbons to a greater extent than propene. With rise in temperature, the inhibiting effect of the additive diminishes.

Stepukhovich and Shver [9, 15] consider that the mechanism of the inhibiting effect of additives on the cracking of paraffins consists in hydrogen abstraction from the CH_3 group of the olefin by the chain propagators (the active radicals H and CH_3) in their collisions with molecules of the inhibiting olefin, a molecule of H_2 or CH_4 being formed together with inactive radicals. The more powerful inhibiting effect of isobutene, as compared with propene, is associated with the presence of two CH_3 groups in isobutene, hydrogen abstraction from which may give an active radical with a long chain [16].

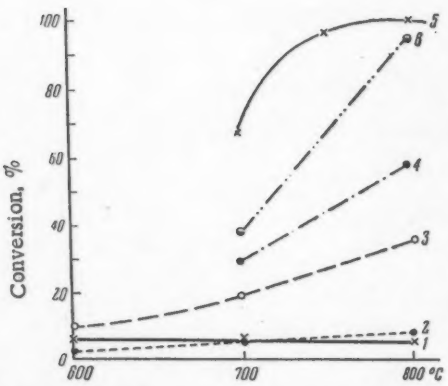

Fig. 1. Dependence of the conversion of heptane on temperature and medium: 1) Na; 2) KOH on KAD; 3) KAD; 4)without metal; 5) Al; 6) Sn.

The retardation of the thermal cracking of hydrocarbons is brought about also by nitric oxide [17, 18]. Even small amounts of nitric oxide have an inhibiting effect on the decomposition of hydrocarbons. With increase in concentration the rate of decomposition falls up to a certain moment, after which further addition of nitric oxide does not bring about any change in rate. An analogous effect is observed in the decomposition of pentane in presence of an inhibiting addition of propene [14]. To explain the incomplete inhibition of the reaction by inhibitors, Hinshelwood and other authors [17-19] suppose that the thermal decomposition of the hydrocarbon proceeds by two parallel mechanisms: chain, which is completely suppressed in presence of an inhibitor, and molecular, which ensures the reaction of an appreciable fraction of the original substance. However, this point of view is not in accord with the results of experiments on the cracking of hydrocarbons in presence of deuterium-containing molecules, which were carried out by Poltarak and Voevodskii [20]; these showed that, both in the pure state and in presence of large amounts of nitric oxide, the thermal decomposition of propane proceeds with the participation of free radicals. It was suggested also that the inhibitor takes part not only in chain termination, but also in chain initiation [12,21], but there is no reason to expect that for different inhibitors the residual rate would be identical, as is in fact observed experimentally. Voevodskii [22] explains this phenomenon on the basis of Semenov's view [23] that the initiation and termination of chains are heterogeneous processes and that change in reaction rate in the course of the transformations and under the action of inhibitors must be associated with change in the surface of the reaction vessel.

In their next investigation they proved that the surface affected the kinetics and rate of the thermal decomposition of propane [24].

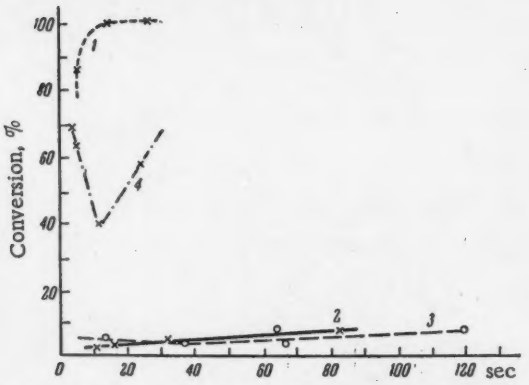

Fig. 2. Relation of heptane at 700° to time of contact with 1) BAU; 2) BAU + KOH; 3) KAD + KOH; 4) tin.

The study of the inhibition of the thermal decomposition of hydrocarbons acquires great scientific and technical importance in view of the fact that in many cases there are now great demands for thermal stability in hydrocarbons under the conditions of their utilization, and to maintain this stability inhibitors are required [25, 26]. It was of interest to study the effect of different metals on the thermal decomposition of hydrocarbons.

We found that the pyrogenetic transformations of heptane proceed selectively depending on the metal or metal compound: sodium and potassium hydroxide retard the decomposition of heptane, whereas aluminum and tin accelerate the cracking reaction (Figures 1 and 2). At 700° with a contact time of 10-20 seconds the extent of the decomposition of heptane falls from 100% to 1% in presence of KOH.

In the present work we studied the transformation of heptane in presence of sodium, potassium hydroxide, aluminum, and tin at atmospheric pressure, and for comparison we give the results also for the cracking of heptane in absence of metals and over KAD and BAU activated charcoals. The experiments were carried out in a flow apparatus [27, 28]. Through a layer of the molten metal or charcoal filling saturated with potassium hydroxide we passed heptane vapor continuously with a definite speed at the given temperature. The reaction products were collected and analyzed.

EXPERIMENTAL

The starting materials were: sodium, density 0.971, m.p. 97.7°; potassium hydroxide, pure reagent, No. 946; commercial aluminum, m.p. 659.8°; tin ingots, m.p. 231.9°; heptane, b.p. 98°, d_4^{20} 0.6850, n_D^{20} 1.3960 (purified by distillation over sodium).

We carried out experiments enabling us to determine the effect of the medium as a function of the temperature of cracking of heptane.

The results (see Figure 1) show a great variation in the effect of the medium on the cracking of heptane, for in presence of aluminum and tin heptane undergoes profound changes: at 800° the conversion attains 100%. On the other hand, sodium and potassium hydroxide have retarding effects and the conversion of heptane reaches only 5-7%; here the temperature of the process does not affect the extent of the conversion of heptane.

The gas from the cracking of heptane in presence of sodium and of KOH differs considerably from the gas from thermal cracking in composition: most (60-85%) of the gas is hydrogen accompanied by a little unsaturated hydrocarbons (Table 1).

In contact with aluminum and with tin heptane gives gaseous and liquid reaction products characteristic of profound pyrolysis; condensation products including carbides are also formed.

In experiments over sodium and potassium hydroxide the heptane cracking condensate obtained consisted of unchanged heptane, i.e., liquid reaction products were not formed under these conditions (Table 2). A retarding effect in presence of sodium and of potassium hydroxide was observed also in the case of the prolonged heating of cyclohexene in an autoclave at 500°; it then remained almost unchanged, whereas in absence of these substances it was converted entirely into a viscous resinous product [28]. The next series of experiments was carried out to determine the effect of the contact time on the conversion of heptane over KOH at 700°.

Comparative experiments on the cracking of heptane over BAU activated charcoal and over potassium hydroxide deposited on the same charcoal show clearly that at 700° with a contact time of 10-20 seconds the extent of the decomposition of heptane falls from 100% to 1% in presence of potassium hydroxide (Fig. 2).

The composition of the gas is independent of the contact time. The specificity of the composition of the gas is preserved both over KOH and in its absence: the predominance of hydrogen in the first case, and a composition

characteristic of gas from the thermal pyrolysis of hydrocarbons in the other. The gas obtained in contact with tin was distinguished by a high content of unsaturated hydrocarbons.

TABLE 1. Composition of the Gas from the Cracking of Heptane

Temp. (°C)	Comp. (% by vol.) C_nH_{2n}	H_2	C_nH_{2n+2}	Sp. gr. of gas
Experiments in an empty reactor				
700	40,4	12,2	47,4	0,89
800	44,0	22,5	34,0	0,77
Experiments with sodium				
700	2,5	83,5	14,0	0,26
750	1,0	84,6	14,4	0,19
800	0,5	83,6	15,9	0,21
Experiments with potassium hydroxide deposited on KAD activated charcoal				
600	6,7	61,7	31,5	0,42
700	5,4	76,3	18,3	0,35
800	7,3	62,7	30,0	0,42
Experiments with KAD activated charcoal				
600	22,9	47,9	29,2	0,63
700	22,5	43,1	34,4	0,57
800	30,0	39,0	31,0	0,70
Experiments with aluminum				
700	50,2	15,3	34,5	0,91
750	42,3	24,2	33,5	0,75
800	36,2	30,5	33,3	0,65
Experiments with tin				
700	54,1	10,6	35,3	0,98
800	55,7	12,4	31,9	0,95

The condensate obtained over potassium hydroxide was almost entirely unchanged heptane, even with a contact time of about two hours, whereas over activated charcoal and tin with a contact time of 10 seconds, heptane was converted completely into gas and condensation products.

TABLE 2. Characteristics of Liquid Cracking Products from Heptane

Temp. of expt.	Fractional composition: up to 98°	98°	above 98°	d_4^{20}	n_D^{20}	Iodine value
Original heptane						
	0	100	0	0,6850	1,3960	0
Experiments in an empty reactor						
700	1,3	85,0	13,7	0,6863	1,3985	15,0
800	5,3	82,4	12,3	0,6882	1,3985	12,0
Experiments with sodium						
700	0	100	0	0,6846	1,3960	1,3
750	0	100	0	0,6820	1,3950	0,8
800	0	100	0	0,6803	1,3980	1,2
Experiments with potassium hydroxide deposited on KAD activated charcoal						
600	0	100	0	0,6854	1,3880	1,5
700	0	100	0	0,6853	1,3880	3,4
800	0	100	0	0,6859	1,3889	4,0
Experiments with KAD activated charcoal						
600	1,0	98,5	0,5	0,6878	1,3890	4,2
700	2,2	96,8	0,6	0,6866	1,3888	11,0
800	3,3	96,0	0,7	0,6849	1,3880	14,0
Experiments with aluminum						
700	15,4	80,0	4,6	0,7031	1,4110	31,8
800	16,0	80,0	14,0	0,8535	1,5470	55,8
Experiments with tin						
700	10	90	0	0,6848	1,3880	21
800	—	—	—	0,7272	1,4100	40

TABLE 3. Cracking of Heptane in Presence of Triisobutylaluminum at 500°.

Temp. (°C)	Rate of feed of starting material (ml/hr)	Catalyst (g/100 ml of heptane and moles/mole of heptane)	Yield (%)		Amt. of heptane decomposed (moles per 100 moles of heptane)
			gas	condensate	
500	106	4 0,03	12,3	81,7	19,6
500	100	0,8 0,006	11,1	88,9	17,3
500	99	1,7 0,013	13,6	83,8	21,6
600	96	1,7 0,013	53,7	21,5	73,4
500	100	4,7 0,035	12,8	87,2	23,8
500	102	Clean reactor	15,0	85,0	22,5
500	103	» »	14,6	85,4	22,0
600	99	» »	78,4	7,3	94,8
500	99	1 g Al	20,9	79,1	28,3
500	100	1 g Al	27,3	72,7	34,1
500	103	2,4 g Al	22,6	77,4	31,1
500	96	1,6 g Al	18,3	81,7	26,5

In view of the above, experiments on the cracking of heptane in presence of triisobutylaluminum were of great interest. The experiments were carried out in a flow apparatus [27, 28]. The catalyst was first dissolved in heptane; the concentration of catalyst varied from 0.006 to 0.35 mole per mole of heptane, or 0.8-4.7 g per 100 ml of heptane. A higher concentration of catalyst brought about the formation of a precipitate and contamination of the tubes when the starting material was pumped into the reactor. Variation within the range of catalyst concentrations used had no substantial effect on the results. Experiments were carried out under the same conditions, but heptane and catalyst were first passed into the reactor, and then the feed to the reactor was switched over to pure heptane. The results were compared with those on the cracking of heptane in a clean reactor under the same conditions.

As will be seen from Table 3, addition of triisobutylaluminum lowered the rate of decomposition of heptane; with rise in temperature to 600° this behavior was still more strongly marked.

It is evident that triisobutylaluminum decomposed with formation of inactive i-C_4H_9 radicals, which retarded the cracking of heptane. Simultaneously, the walls of the reactor were covered with a thin layer of aluminum, which has an accelerating action on the cracking of heptane. A little aluminum (1 g) increases the rate of cracking of heptane by 30%.

SUMMARY

1. It was found that the pyrogenetic transformations of heptane in the molten metals aluminum, tin, and sodium proceed selectively in a way dependent on the nature of the metal.

2. Aluminum and tin accelerate the cracking of heptane. Sodium and potassium hydroxide exert a powerful retarding action on the cracking of heptane.

3. The mechanism of the action of inhibiting additives appears to amount to chain termination due to the reaction of alkali metals with free radicals or to the saturation of hydrogen liberated by reaction with hydrocarbons.

4. Alkali-metal hydroxides may be reduced by hydrocarbons to metals, which then react by the mechanism indicated.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

SYNTHESIS OF TRI- AND TETRA-PHENYLALKANES AND STUDY OF THEIR HYDROGENATION

M. A. Chel'tsova and A. D. Petrov

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR
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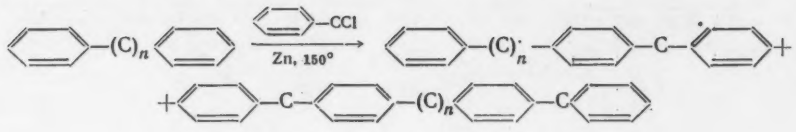
In previous investigations [1-3], by organomagnesium synthesis we have prepared various di- and tri-phenylalkanes and carried out their selective hydrogenation under various conditions of temperature and pressure over Ni and PtO_2 catalysts [4, 5]. With the object of determining the relation between the structures of the hydrocarbons and their properties, for all the hydrocarbons that we obtained we determined their physicochemical properties, including freezing point, viscosity, and thermal-oxidative stability.

In the present work we synthesized tri- and tetra-phenylalkanes such that paraffin chains present in their molecules were disposed between benzene rings. We considered that hydrocarbons of this type should have enhanced stability to thermal oxidation. The selective hydrogenation of these hydrocarbons enabled us to pass to mixed hydrocarbons, which generally had lower freezing points than the original aromatic hydrocarbons or the corresponding hydrocarbons of the naphthene series. Hydrocarbons containing paraffin links between benzene rings were prepared by the alkylation of bibenzyl and 1,3-diphenylpropane with benzyl chloride [6] in accordance with the scheme:



in which n=2 and 3.

The yield of tricyclic hydrocarbons was 50%, and that of tetracyclic hydrocarbons was 20%.

To isolate them in a pure state the resulting substances were subjected to fractional distillation and to chromatographic separation on a column of ASM silica gel (height of lower part of column 56.5 cm, diameter 1.0 cm; height of the upper part 42.0 cm, diameter 2.2 cm; amount of silica gel 150 g). The structures of the hydrocarbons obtained were were established by their physicochemical properties (Table 1), their infrared spectra (Figures 1-9), and the products obtained on their oxidation with chromium trioxide in acetic acid.

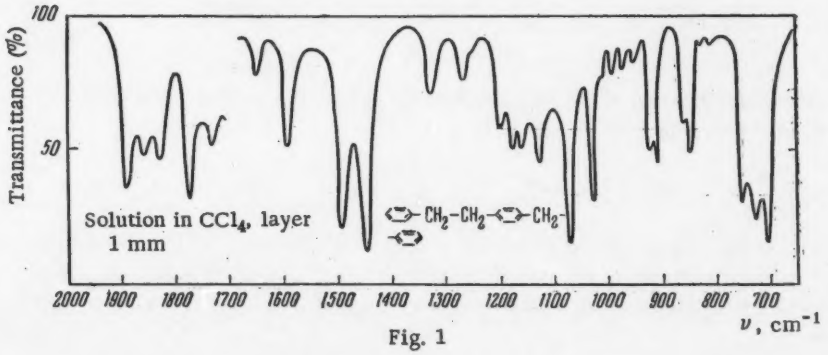


Fig. 1

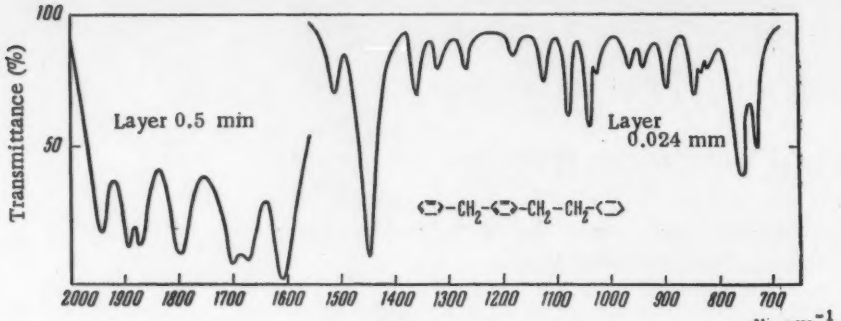


Fig. 2

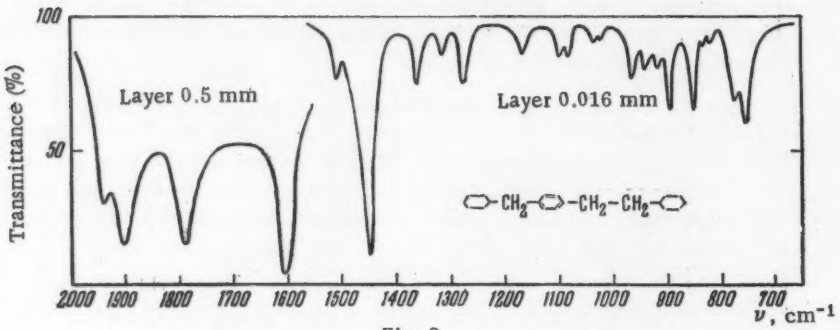


Fig. 3

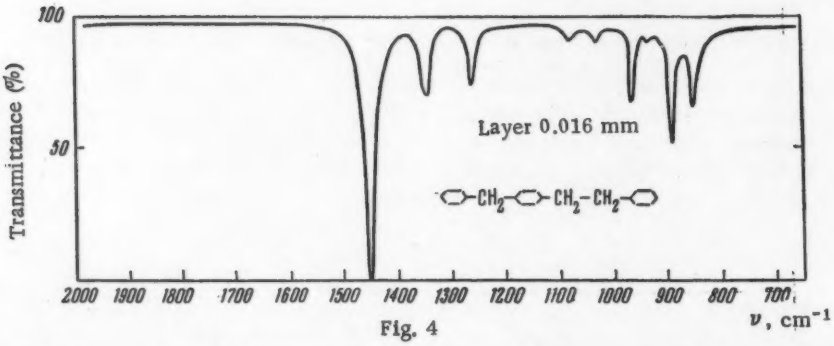
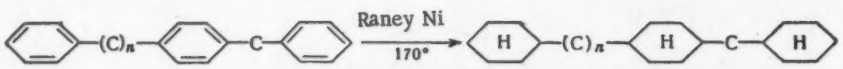
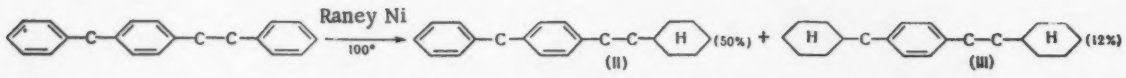


Fig. 4

The complete hydrogenation of the hydrocarbons was carried out in presence of hydrogen under pressure in an autoclave at 170° over Raney nickel:



In this case we did not observe the partial formation of dicyclohexylalkanes, which are usually obtained in the hydrogenation of alkyltriphenylmethanes as a result of the elimination of one of the rings. The incomplete hydrogenation of 1-p-benzylpehnyl-2-phenylethane (I), which we obtained by the alkylation of bibenzyl with benzyl chloride, proceeded as follows



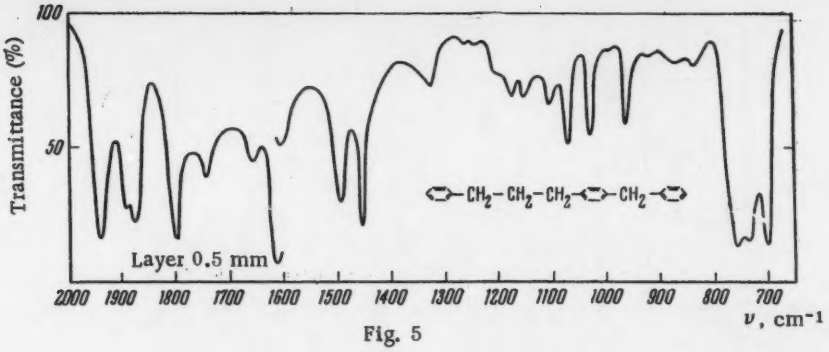


Fig. 5

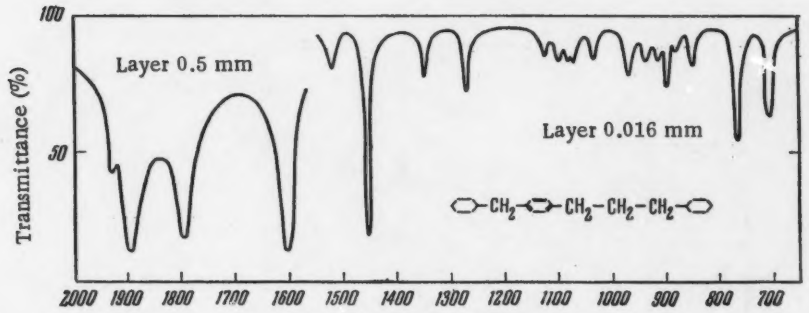


Fig. 6

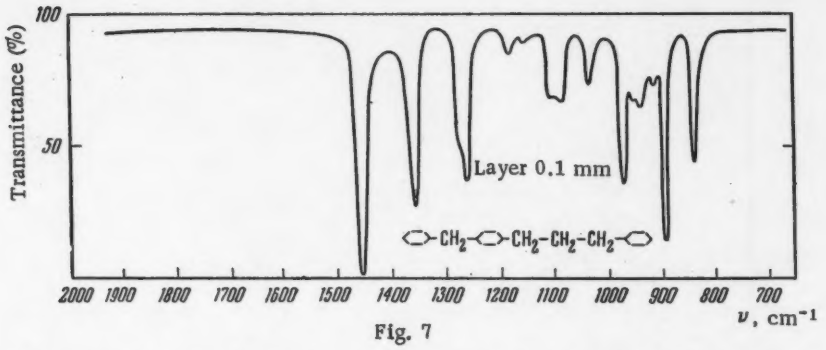
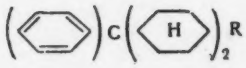


Fig. 7

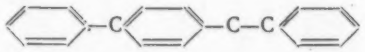
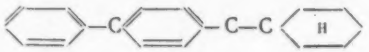
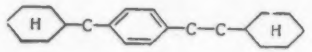
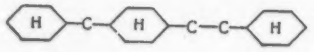
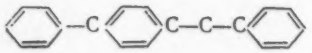
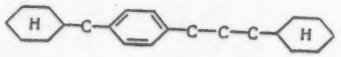
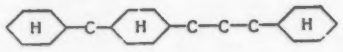
with the formation mainly of 1-p-benzylphenyl-2-cyclohexylethane (II), i.e., the reaction stopped at the stage of the hydrogenation of one ring. In the case of the incomplete hydrogenation of triphenylalkanes of the type $(C_6H_5)_3CR$, in which $R = C_4 - C_{10}$, hydrogenation always goes as far as the formation of hydrocarbons of the type [4]



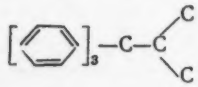
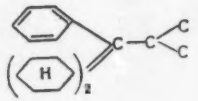
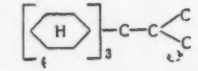
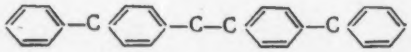
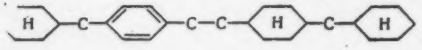
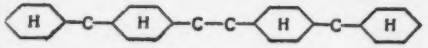
i.e., two benzene rings are hydrogenated.

With the object of making a qualitative assessment of the hydrogenatability of hydrocarbons of different types, we hydrogenated the following under identical conditions (in a long-necked flask over PtO_2 at room temperature):

TABLE 1

No.	Formula of hydrocarbon	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	MR found	MR calc.	Found (%) C	Found (%) H	Molecular formula	Calc. (%) C	Calc. (%) H
I*		(M.p. 43°)	—	—	—	—	92,59 92,34	7,25 7,34	$C_{21}H_{20}$	92,58	7,42
II		140—142 (0,5)	0,9862	1,5550	90,67	89,78	89,64 89,70	9,38 9,34	$C_{21}H_{26}$	90,55	9,45
III		148—150 (0,5)	0,9480	1,5240	91,76	91,18	89,06 88,81	11,18 11,17	$C_{21}H_{32}$	88,64	11,36
IV		180—181 (1,0)	0,9134	1,4949	92,66	92,58	86,93 86,98	13,23 13,36	$C_{21}H_{38}$	86,78	13,22
V		218 (4,0)	—	—	—	—	92,30 92,32	7,73 7,69	$C_{22}H_{22}$	92,25	7,75
VI		226—227 (4)	0,9485	1,5260	96,54	95,80	87,77 87,66	10,90 10,90	$C_{22}H_{54}$	88,50	11,50
VII		227 (4)	0,9126	1,4940	97,10	97,20	86,03 86,24	12,91 12,91	$C_{22}H_{40}$	86,27	13,27

(Table 1, cont.)

No.	Formula of hydrocarbon	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	MR found	MR calc.	Found (%) C	Found (%) H	Molecular formula	Calc. (%) C	Calc. (%) H
VIII**		(M.p. 91°)	—	—	—	—	92,03 92,01	7,82 7,75	$C_{22}H_{22}$	92,24	7,76
IX		220—221 (0,5)	d_4^{40} 0,9711 d_4^{4} 0,9592	n_D^{40} 1,5330 n_D^{4} 1,5280	95,34	95,79	88,72 88,65	11,17 11,21	$C_{22}H_{34}$	88,50	11,50
X		190 (4,0)	d_4^{40} 0,9454 d_4^{4} 0,9323	d_4^{40} 1,5100 d_4^{4} 1,5040	96,68	97,20	86,93 87,19	13,00 12,90	$C_{22}H_{40}$	86,73	13,27
XI		254 (1,0) M.p. 72°	—	—	—	—	92,74 92,79	7,30 7,09	$C_{28}H_{26}$	92,74	7,26
XII		212 (0,5)	0,9614	1,5300	122,2	121,3	88,21 88,46	11,64 11,56	$C_{28}H_{44}$	88,33	11,67
XIII		252 (1,0)	0,9360	1,5050	122,5	122,7	86,60 86,87	13,13 12,86	$C_{28}H_{50}$	86,93	13,07

* Characterized by Fuson [6] as a liquid substance.

** Characterized by Gomberg [7] as a liquid substance.

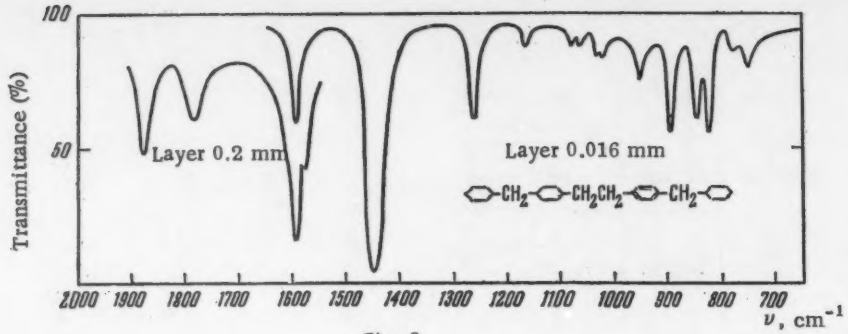


Fig. 8

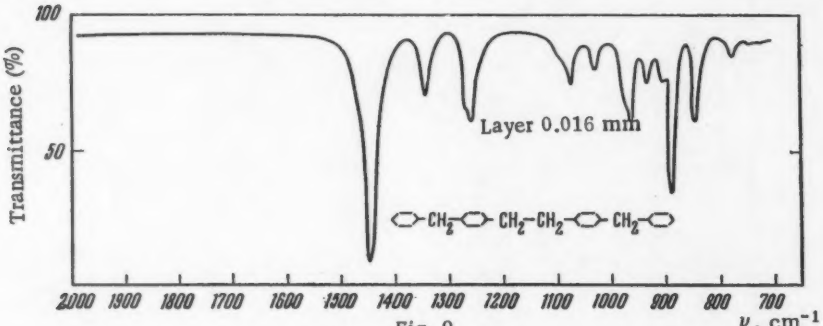


Fig. 9

1,7-diphenyl-4-(3-phenylpropyl)heptane, (I), and 1,1,1-triphenylheptane. It was found that under the given conditions the last hydrocarbon was not hydrogenated at all and the first two were hydrogenated to give hydrocarbons containing two aromatic and one hydroaromatic ring in the molecule; 1,7-diphenyl-4-(3-phenylpropyl)heptane was hydrogenated about 2.5 times as readily (fast) as (I).

TABLE 2

Hydrocarbon No.	M.p. (f.p.) (°C)	Viscosity (centipoise) at				
		0	20°	50°	100°	150°
I	43 cryst.	—	—	10,87	3,95	2,42
II	—40 glass	212,8	48,49	12,48	3,58	1,73
IV	—28 glass		238,0	33,22	6,06	2,53
V	42 cryst.	—	—	9,88	3,20	1,59
VI	—33 glass	835,05	136,97	25,14	5,45	2,31
VII	—25 glass	1 306,4	177,78	30,73	6,35	2,57
VIII	91 cryst.	—	—	—	—	—
IX	6 glass	—	—	—	8,46	2,01
X	8 glass	—	—	395,08	14,37	3,53
XI	72 cryst.	—	—	—	—	—
XII	7 glass	—	—	666,2	30,98	6,7
XIII	—2 glass	—	24 030,0	409,1	25,6	6,35

In order to determine the effect of the structures of hydrocarbons of a given composition on their properties, by the organomagnesium method we synthesized 2-methyl-1,1,1-triphenylpropane (VIII) [7] and carried out its complete and incomplete hydrogenation to 1,1,1-tricyclohexyl-2-methylpropane (X) and 1,1-dicyclohexyl-1-2-methyl-1-phenylpropane (IX).

Table 2 gives the melting points of the hydrocarbons and their viscosity properties at various temperatures. Comparing the data in Table 2, we see that the hydrocarbons of mixed structure have the lower melting (or freezing) points. Thus, (I) melts at 43°, but a hydrocarbon of the same structure, but with two aromatic and one hydroaromatic ring (II), freezes at −40°. 1,2-Bis-p-benylethane (XI) has m.p. 72°, but a hydrocarbon of the same structure but with one aromatic and three hydroaromatic rings, freezes at 7°.

The melting points and viscosities of hydrocarbons of given composition, but different structure [(V) and (VIII), (VI) and (IX), (VII) and (X)], vary considerably.

EXPERIMENTAL*

1-Cyclohexyl-2-[4-(cyclohexylmethyl)cyclohexyl]ethane (IV) was prepared from (I) by its hydrogenation over Raney nickel at 170° in presence of hydrogen under pressure. The hydrocarbon was identified by its physicochemical properties and infrared spectrum. The hydrocarbon (I) was prepared [6] by the addition of a little (1-2 g) of zinc dust to a mixture of 40 g (0.22 mole) of bibenzyl and 28 g (0.22 mole) of benzyl chloride heated to 150° for one hour, after which the contents of the flask were immediately distilled under reduced pressure. We then obtained about 15-17 g (about 50%) of (I), whose structure was established by means of its infrared spectrum and its oxidation to p-benzoylbenzoic acid, m.p. 192°, and benzoic acid, m.p. 118°, undepressed by admixture of known benzoic acid. For p-benzoylbenzoic acid the literature [6] gives m.p. 194°.

The experiment was repeated several times, and we obtained 190 g of (I) and 98 g of a higher fraction, b.p. 230-245° (0.5 mm).

The hydrocarbon (II) was prepared in two ways: 1) 42 g of (I) was hydrogenated over Raney nickel at 100° in presence of hydrogen under pressure until hydrogen ceased to be absorbed. The hydrogenation product was subjected to fractional distillation and chromatographic separation. We isolated 10 g of the original hydrocarbon, 15 g of the hydrocarbon (II), and 5 g of 1-cyclohexyl-2-p-(cyclohexylmethyl)phenylethane (III). The hydrocarbon (II) was identified by the infrared spectrum and its oxidation with chromium trioxide to p-benzoylbenzoic acid. The hydrocarbon (III) was identified by the infrared spectrum.

2) 17 g of (I) was hydrogenated in presence of 0.146 g of PtO_2 at room temperature and atmospheric pressure. By fractional distillation and chromatographic purification of the hydrogenation product we obtained 9.2 g of (II).

30 g of (I) was hydrogenated over Raney nickel at 170° under a pressure of hydrogen until absorption ceased. After fractional distillation and separation on a chromatographic column we isolated 26 g of (IV).

The hydrocarbon (XI) (73 g; m.p. 72°) was isolated from the fraction of b.p. 230-245° (0.5 mm) (obtained in the alkylation of bibenzyl with benzyl chloride) by fractional distillation and repeated purification through a chromatographic column. The resulting hydrocarbon was identified by oxidation to p-benzoylbenzoic acid.

1,2-Bis-4-(cyclohexylmethyl)cyclohexylethane (XIII) was prepared from 45 g of (XI) by its hydrogenation over 10 g of Raney nickel at 170-180° in presence of hydrogen under pressure until hydrogen ceased to be absorbed. The hydrogenation product (42 g) was subjected to repeated fractional distillation and separation on a chromatographic column; we then isolated 19.5 g of (XIII) and 6.3 g of 1-[4](cyclohexylmethyl)cyclohexyl]-2-[4-(cyclohexylmethyl)-phenyl]ethane (XII), a hydrocarbon of mixed structure whose molecule contains three hydroaromatic and one aromatic ring.

1-p-Benzylphenyl-3-phenylpropane (V) was prepared as follows. From 346 g of $C_6H_5CH_2CH_2Br$, 48 g of magnesium, and 170 g of benzaldehyde we prepared 170 g (74%) of 1,3-diphenyl-1-propanol; b.p. 208−212° (20 mm); n_D^{20} 1.5750. The literature [8] gives b.p. 192-194° (12 mm). The synthesis of the alcohol was repeated and, in all, we obtained about 400 g. The alcohol was dehydrated by Ziegler's method [9] and we obtained 183 g (42%) of 1,3-diphenylpropene; b.p. 180−181° (15 mm); n_D^{20} 1.5980; d_4^{20} 1.0064. The literature [8] gives: b.p. 313° (760 mm); n_D^{20} 1.6000; d_4^{20} 1.0061.

The unsaturated hydrocarbon was hydrogenated over PtO_2 in ethanol. The catalyzate was distilled through a column of 18-plate efficiency. We isolated 162 g (88%) of 1,3-diphenylpropane; b.p. 163° (19 mm); n_D^{20} 1.5600; d_4^{20} 0.9802. The literature [10] gives: b.p. 297° (760 mm); n_D^{20} 1.5594; d_4^{20} 0.97996.

The alkylation of 1,3-diphenylpropane was carried out under the conditions described for the alkylation of bibenzyl with benzyl chloride. From 140 g of 1,3-diphenylpropane and 91 g of benzyl chloride we obtained 101.5 g

*V. P. Krukhtanova took part in the experimental work.

(50%) of (V). After fractional distillation and purification through a chromatographic column, the hydrocarbon was identified by its infrared spectrum and oxidation to benzoylbenzoic and benzoic acids. 22 g of (V) was hydrogenated at 170° under a pressure of hydrogen. From 20 g of the hydrogenation product we isolated 14 g of 1-cyclohexyl-3-[4-(cyclohexylmethyl)cyclohexyl]propane (VII).

(V) (30 g) was hydrogenated over Raney nickel at 100° in presence of hydrogen under pressure until the absorption of hydrogen ceased. The hydrogenation product was subjected to fractional distillation and chromatographic separation. We isolated 13 g of 1-cyclohexyl-3-p-(cyclohexylmethyl)phenylpropane (VI) and 14 g of (VII).

The hydrocarbon (VIII)* was prepared in an amount of 253 g (50%) from 248 g of isopropyl bromide, 48 g of magnesium, and 445 g of chlorotriphenylmethane; b.p. 195-200° (1 mm). After chromatographic purification (IX) was isolated in the crystalline state, m.p. 91°.

The resulting hydrocarbon (64 g) was hydrogenated over Raney nickel at 120° in presence of hydrogen under pressure until the absorption of hydrogen ceased. The hydrogenation product was subjected to chromatographic separation, as a result of which we obtained (IX) (7 g; 12%) and (VIII) (41 g; 70%).

(VIII) (50 g) was hydrogenated over Raney nickel at 170-180° in presence of hydrogen under pressure. The hydrogenation product (48 g) was subjected to chromatographic purification until the refractive index was constant. We obtained 18.5 g of (X) (37%) and 17 g (34%) of 1,1-dicyclohexyl-2-methylpropane.

The authors express their great thanks to E. V. Lubush for the spectrographic investigation of the hydrocarbons that we prepared.

SUMMARY

1. The following previously undescribed hydrocarbons were prepared and characterized by their freezing points, viscous properties, and infrared spectra: 1-p-benzylphenyl-2-cyclohexylethane, 1-cyclohexyl-2-[4-(cyclohexylmethyl)cyclohexyl]ethane, 1-cyclohexyl-2-p-(cyclohexylmethyl)phenylethane, 1,2-bis-p-benzylphenylethane, 1-[4-(cyclohexylmethyl)cyclohexyl]-2-p-(cyclohexylmethyl)phenylethane, 1,2-bis-4-(cyclohexylmethyl)cyclohexylethane, 1-p-benzylphenyl -3-phenylpropane, 1-cyclohexyl-3-p-(cyclohexylmethyl)phenylpropane, 1-cyclohexyl-3-[4-(cyclohexylmethyl)cyclohexyl]propane, 1,1-dicyclohexyl-2-methyl-1-phenylpropane, and 1,1,1-tricyclohexyl-2-methylpropane.

2. In the case of 1-p-benzylphenyl -2-phenylethane, hydrogenation over Raney nickel and over PtO_2 stops at the stage of the hydrogenation of one ring, whereas in the hydrogenation of 1,1,1-triphenylalkanes over Raney nickel not less than two rings are hydrogenated. Over PtO_2 hydrocarbons of this type are not hydrogenated at all.

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* The graudate U Chzhun-yui took part in the synthesis and hydrogenation of this hydrocarbon.

VINYL COMPOUNDS IN THE DIENE SYNTHESIS

COMMUNICATION 9. SOME PROPERTIES OF ADDUCTS IN DIENE CONDENSATIONS WITH VINYL SULFIDES

M. F. Shostakovskii, A. V. Bogdanova, and T. M. Ushakova

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR
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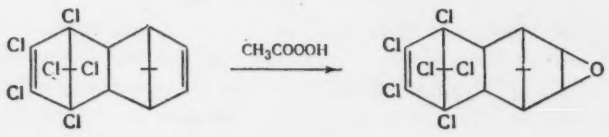
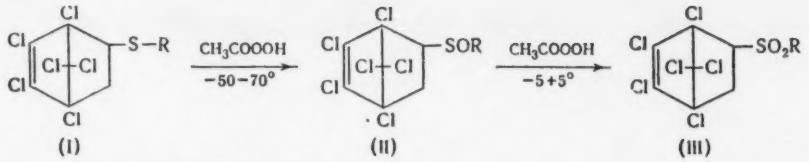
We showed previously [1] that vinyl sulfides may be used successfully in the diene-synthesis reaction with cyclopentadiene (CPD) and with hexachlorocyclopentadiene (HCCPD). In the present case we were interested in the properties of the adducts obtained, which contain a bivalent sulfur atom; for this purpose we investigated the oxidation of the adducts and their reaction with mercuric chloride. The oxidation was carried out with peroxyacetic acid, which is a convenient, mild oxidizing agent. The literature describes examples of the preparation of sulfoxides and sulfones by the oxidation of sulfides with peroxyacetic acid [2].

The adducts obtained from HCCPD contain an inactive chlorinated double bond in the ring, and the reactions of such compounds usually proceed without touching this bond. Thus, in the oxidation of aldrin with peroxyacetic acid, only the unsubstituted double bond undergoes epoxide formation [3].



Hence, the oxidation of the adducts (I) of vinyl sulfides with HCCPD by means of peroxyacetic acid must also proceed without touching the chlorinated double bond and lead to the formation of the corresponding sulfones, as was shown for the case of the adduct with ethyl vinyl sulfide (Ia) [4]. By detailed study of the conditions of this reaction we found that it proceeds stepwise in two stages.



(I) (II) (III)

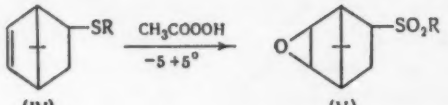
R=C_2H_5 (a); C_4H_9 (b); C_6H_5 (c)

For the first stage, i.e., oxidation of the adduct to the sulfoxide (II), mild conditions are sufficient (cooling the mixture to from −50° to −70° for five hours), and the second stage, i.e., oxidation of the sulfoxide to the sulfone (III), requires more severe conditions (excess of peroxyacetic acid for a longer time at from −5° to + 5°). The conditions found for the preparation of sulfones and sulfoxides ensure the formation of these compounds as main reaction products and were used equally successfully for the oxidation of sulfides containing alkyl (Ia and Ib) and aryl (Ic) groups. The oxidation reaction enabled us to prepare some crystalline derivatives of hexachlorobicycloheptenyl sulfides.

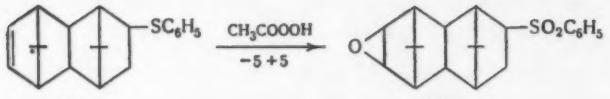
We recently showed [5] that the diene-synthesis adducts of aryl vinyl ethers with CPD are mixtures of two isomeric forms of endo and exo configurations; with rise in the temperature of the mixture the content of the exo form increases. It was natural to suppose the existence of similar regularities for the adducts of vinyl sulfides with HCCPD [1]. To resolve this matter we synthesized these adducts in two ways. In the first case we carried out either the diene

condensation or the isolation of the adducts with heating; in the second case the synthesis was carried out at room temperature [4] and methods not requiring heating (chromatography) were used in the isolation of the products. It was found, however, that the melting points of the crystalline adducts of phenyl vinyl sulfide with HCCPD (Ic), and also their sulfones (IIIc), prepared by the first and second methods were identical. For the adducts formed with butyl vinyl sulfide (Ib), also synthesized by two methods, we compared the melting points of their crystalline derivatives, the sulfones (IIIb), but in this case also they did not differ from one another. Also, heating of the sulfone (IIIa) for five hours at 140-150° again did not lead to change in melting point. On the basis of these facts we may suppose that in the case of the adducts of vinyl sulfides with HCCPD (I) ready thermal isomerization of one isomeric form into the other does not occur under the conditions investigated; they are probably pure endo forms. The adducts of vinyl sulfides with CPD (IV-VI) contain an unsubstituted active double bond in the ring; hence in their reaction with peroxyacetic acid under the usual conditions, together with the oxidation of the sulfide group to a sulfone group, epoxide formation occurs at the double bond.

The epoxy sulfones (Va, Vb, VII) were obtained in good yields for sulfides both of the norbornene series (IVa and IVb) and of the dimethanonaphthalene series (VI).



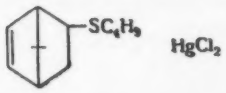
(IV) (V)



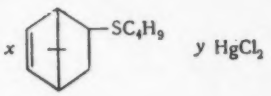
(VI) (VII)

R=C_4H_9 (a); C_6H_5 (б)

A characteristic of sulfides is their ability to form crystalline complexes with mercury salts, but the use of these compounds for identification is often rendered difficult by the fact that a given sulfide may give complexes with different proportions of the other component [2b]. We studied the reaction of 5-(butylthio)-2-norbornene (IVa) with aqueous and alcoholic solutions of mercuric chloride. On treatment of the sulfide with aqueous mercuric chloride at room temperature we obtained an 85% yield of a stable crystalline product of the addition of one mercuric chloride molecule to a molecule of adduct



with some admixture of complexes, probably differing in the proportions of the components



The reaction of the sulfide with alcoholic mercuric chloride under analogous conditions led to the formation of a mixture of complex salts from which we isolated the complex (VIII) and a complex of more complicated structure (X), containing eight mercuric chloride molecules to five molecules of the sulfide. As would be expected [6], the complex salts formed decomposed with the liberation of hydrogen chloride, which could be titrated with 0.1 N NaOH in presence of Methyl Orange.

EXPERIMENTAL

Condensation of Vinyl Sulfides with HCCPD by the Fist Method. Equimolecular amounts of butyl vinyl sulfide (3.6 g; 0.03 mole) and HCCPD (8.1 g; 0.03 mole) were sealed in a tube (hydroquinone!) and left for 39 days. After fractionation of the reaction mixture we obtained 7.8 g (87.3% on the 6.6 g of diene that reacted) of 5-(butylthio)-1,2,3,4,7,7-hexachloro-2-norbornene (Ib); b.p. 135-137° ($9 \cdot 10^{-2}$ mm); n_D^{20} 1.5537; d_4^{20} 1.4592; found MR 85.41. $C_{11}H_{12}Cl_6S$. Calculated MR 84.97. Found: C 33.92; 33.85; H 3.16; 3.06; Cl 54.70, 54.70; S 7.92; 8.43%. $C_{11}H_{12}Cl_6S$. Calculated: C 33.96; H 3.11; Cl 54.70; S 8.24%. Also (Ib) was synthesized in 84% yield by heating a mixture of the reactants to 100° for three hours [1], and it had similar constants.

From a mixture of 4.2 g (0.03 mole) of phenyl vinyl sulfide and 8.1 g (0.03 mole) of HCCPD that had stood at room temperature for 30 days, vacuum fractionation gave 6.8 g (75% on the 6.0 g of diene that reacted) of 5-(phenylthio)-1,2,3,4,7,7-hexachloro-2-norbornene (Ic), m.p. 41-42°.

Condensation of Vinyl Sulfides with HCCPD by the Second Method. (Ic) was isolated from the reaction mixture obtained by the method described for the previous experiment with the aid of chromatography of the petroleum ether solution on alumina; it had m.p. 40-41.5°. A mixture with the adduct (Ic) prepared by us earlier [1] (m.p. 41-42°) melted without depression.

Oxidation of Vinyl Sulfide Adducts of HCCPD, Prepared by the First Method, to Sulfoxides. A flask was charged with 1 g of (Ic) in 40 ml of dry ether, the solution was cooled to from −50° to −70°, and 0.6 ml of peroxyacetic acid was added dropwise. Stirring was continued at this temperature for 5-6 hours. The reaction mixture was then washed with saturated sodium carbonate solution and with water, and was dried with sodium sulfate. Solvent was vacuum-distilled off, and we obtained 0.6 g (60%) of crystalline 5-(phenylsulfinyl)-1,2,3,4,7,7-hexachloro-2-norbornene (IIc), m.p. 93-95° (from petroleum ether. Found: C 36.77; 36.80; H 1.98; 1.98; Cl 50.06; S 7.32; 7.27%. $C_{13}H_8Cl_6SO$. Calculated: C 36.73; H 1.90; Cl 50.06; S 7.54%.

Under the above-described conditions from 1 g of (Ib) we obtained 0.57 g (58%) of 5-(butylsulfinyl)-1,2,3,4,7,7-hexachloro-2-norbornene (IIb), m.p. 143-144° (from aqueous ethanol). Found: C 32.50; 32.39; H 3.05; 2.83; Cl 52.53; S 8.04; 8.06%. $C_{11}H_{12}Cl_6SO$. Calculated: C 32.6; H 2.99; Cl 52.53; S 7.92%.

Analogously, from 1.2 g of (Ia) we synthesized 0.7 g (60%) of 5-(ethylsulfinyl)-1,2,3,4,7,7-hexachloro-2-norbornene, m.p. 118.5-119.2° (from aqueous ethanol). The literature [4] gives m.p. 122-122.5°.

Oxidation of Vinyl Sulfide Adducts of HCCPD, Prepared by the First Method, to Sulfones. The reaction was carried out under the usual conditions in dry ether solution with cooling to from −5° to 0° for 24 hours in presence of excess of peroxyacetic acid.

From 1 g of (Ib) we obtained 0.88 g (82%) of 5-(butylsulfonyl)-1,2,3,4,7,7-hexachloro-2-norbornene (IIIb), m.p. 123-124° (from aqueous ethanol) Found: C 31.35; 31.36; H 3.09; 3.00%. $C_{11}H_{12}Cl_6SO_2$. Calculated: C 31.37; H 2.87%.

Oxidation of 1 g of (Ic) gave 0.81 g (73%) of 5-(phenylsulfonyl)-1,2,3,4,7,7-hexachloro-2-norbornene (IIIc), m.p. 124-126° (from petroleum ether). Found: C 35.54; 35.41; H 2.06; 1.79; Cl 48.25; 48.25; S 7.07; 7.25%. $C_{13}H_8Cl_6SO_2$. Calculated: C 35.40; H 1.83; Cl 48.25; S 7.27%.

Oxidation of Vinyl Sulfide Adducts of HCCPD, Prepared by the Second Method, to Sulfones. The adduct (Ib) prepared at room temperature was not separated from unchanged reactants, but was oxidized to the sulfone. At the end of the reaction the ethereal solution was cooled to from −70° to −80°. The precipitate that then formed was rapidly separated, and was washed, first with water and then repeatedly with petroleum ether, to remove unchanged reactants; it was then dried. The product had m.p. 122-123.5°, undepressed in admixture with the sulfone (IIIb) obtained in Expt. 4. (Ic), prepared analogously, was also oxidized in presence of unchanged reactants. To isolate the oxidized adduct the reaction mixture was dissolved in benzene and twice chromatographed on alumina. The product had m.p. 124-126°, undepressed in admixture with the sulfone (IIIc) obtained in Expt. 4.

Oxidation of Adducts of Vinyl Sulfides with CPD. The oxidation was carried as far as the sulfones with excess of peroxyacetic acid at from −5° to 0° for 24 hours.

From 3 g of (IVa) we obtained 1.9 g (50%) of a very thick colorless noncrystallizing product, b.p. 125-127° ($1 \cdot 10^{-3}$ mm) and n_D^{20} 1.5090; it was found to be 5-(butylsulfonyl)-2,3-epoxynorbornane (Va). Found: C 57.18; 57.24; H 7.74; 7.56; S 13.93; 13.75%. $C_{11}H_{18}SO_3$. Calculated: C 57.36; H 7.88; S 13.92%.

By the oxidation of 1 g of (IVb) we obtained 0.71 g (58%) of 5-(phenylsulfonyl)-2,3-epoxynorbornane (Vb), m.p. 82.5-84° (from petroleum ether). Found: C 62.30; 62.42; H 5.89; 5.98; S 12.89; 12.87%. $C_{13}H_{14}SO_3$. Calculated: C 62.36; H 5.64; S 12.81%.

2,3-Epoxydecahydro-6-(phenylsulfonyl)-1,4:5.8-dimethanonaphthalene (VII) was prepared in 59% yield (0.31 g) from 0.5 g of (VI) and had m.p. 164.5-165.8° (from benzene-methanol mixture). Found: S 9.88. 9.94%; $C_{18}H_{20}SO_3$. Calculated: S 10.14%.

Reaction of 5-(butylthio-2-norbornene (IVa) with Mercuric Chloride Solution. A flask was charged with 0.39 g of the sulfide (IVa) in 10 ml of water, and 16 ml of saturated aqueous mercuric chloride (0.75 g of $HgCl_2$) was added.

There was an immediate precipitate, but to complete reaction the contents of the flask were stirred mechanically for two days at room temperature. We obtained 0.83 g [for (VIII) the yield would be 85.0%] of a white crystalline precipitate, very soluble in alcohol, benzene, acetone, ether, and carbon tetrachloride. Repeated crystallizations from aqueous alcohol and then petroleum ether gave a fraction of m.p. 70-72°, for which the elementary analysis was: C 28.09; 28.01; H 3.88; 3.98% $C_{11}H_{18}SHgCl_2$. Calculated: C 29.10; H 4.00%. This corresponds approximately to the complex (VIII).

To 0.34 g of (IVa) we added 6 ml of a 20% alcoholic solution of mercuric chloride (threefold excess). A precipitate immediately began to form. The mixture was shaken mechanically for two days at room temperature. The crystalline precipitate was filtered off (0.70 g). By three crystallizations from aqueous ethanol we isolated a complex salt of m.p. 157-159.5° (decomp.). Found: C 21.51; 21.41; H 3.27; 3.29%. $(C_{11}H_{18}S)_3(HgCl_2)_8$. Calculated: C 21.41; H 2.93.

The complex salt (VIII), which is readily soluble in alcohol, separated on addition of water to the filtrate remaining after the separation of the precipitate. We obtained 0.32 g of a crystalline product, m.p. 65-72° (from petroleum ether). In the reaction of mercuric chloride in alcohol with (IVa) in presence of Methyl Organe the solution becomes pink. In the titration of 0.1691 g of (IVa) in 6 ml of 20% alcoholic mercuric chloride we required 5.1 ml of 0.1 N NaOH, which corresponds to 55% conversion of (IVa).

SUMMARY

1. A study was made of the peroxyacetic acid oxidation of the adducts formed by aryl vinyl and alkyl vinyl sulfides with hexachlorocyclopentadiene and with cyclopentadiene. The conditions were found for the preparation of sulfoxides or sulfones in high yields as main reaction products.

2. The adducts formed by vinyl sulfides with hexachlorocyclopentadiene are probably pure endo isomers and do not readily undergo thermal isomerization into the exo form.

3. When 5-(butylthio)-2-norbornene is treated with mercuric chloride solutions complex salts between different proportions of sulfide and mercuric chloride are formed.

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COPOLYMERIZATION OF 1-VINYL-2-PYRROLIDINONE WITH METHYL METHACRYLATE AND WITH ACRYLONITRILE

M. F. Shostakovskii, A. M. Khomutov, and F. P. Sidel'kovskaya

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR
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1-Vinyl-2-pyrrolidinone readily polymerizes by the free-radical mechanism and its polymers have valuable properties. The copolymerization of 1-vinyl-2-pyrrolidinone has received little study. There are some data in the literature, mainly in patents, on the copolymerization of 1-vinyl-2-pyrrolidinone with vinyl acetate, maleic anhydride, styrene, diethylene glycol, vinyl laurate, acrylonitrile, methyl methacrylate, vinylsilanes, and methacrylamide [1]. We have studied the copolymerization of 1-vinyl-2-pyrrolidinone with methyl methacrylate and with acrylonitrile. These copolymerizations were carried out at different molar ratios at high conversions. The relations between the concentrations of monomers taken and the yield of copolymer and the proportions of monomer units in the copolymer are shown in Figures 1 and 2. Fig. 1 shows that the copolymerization of 1-vinyl-2-pyrrolidione with methyl methacrylate in presence of azodiisobutyronitrile proceeds with the formation of copolymers in which the

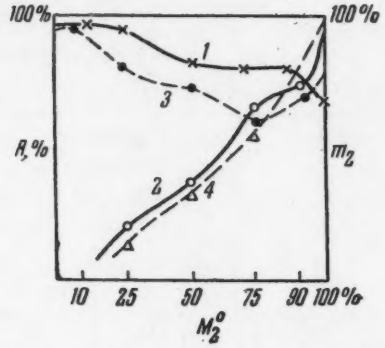

Fig. 1. Relations between the original concentrations of methyl methacrylate, 1-vinyl-2-pyrrolidinone (VP), and N-vinylcaprolactam (VCL) and the yields (A%) and compositions (m_2, moles %) of their copolymers: 1) A% for VP; 3) A% for VCL; 2) m_2 for VP units; 4) m_2 for VCL units. M^0_2 is the original concentration (moles %) of VP or VCL.

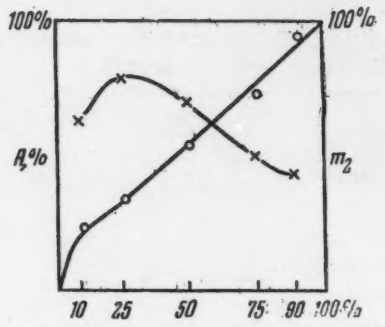

Fig. 2. Effect of 1-vinyl-2-pyrrolidinone concentration on the yield (A%) of copolymer and the proportion of its units (m_2, moles %) in the copolymer in its copolymerization with acrylonitrile. M^0_2 is the original concentration of VP (moles %).

proportion of vinylpyrrolidinone units increases in the concentration of its monomer in the reaction mixture, while the yield of copolymer falls somewhat. When this copolymerization is compared with that of N-vinylcaprolactam with the same monomer in presence of the azo dinitrile it is found that the same relation holds between the vinyl lactam concentration, the proportion of its units in the copolymer and the yield (Fig. 1) [2]. The same relation holds also for the copolymers of 1-vinyl-2-pyrrolidinone and acrylonitrile: with increase in the concentration of vinylpyrrolidinone monomer in the reaction mixture, the yield falls somewhat, but the proportion of vinylpyrrolidinone monomer units in the copolymer rises (Fig. 2).

To form an estimation of the relative activities of the radicals of the monomers studied we determined the copolymerization constants r_1 and r_2 by a graphical method with use of the integral equation of Mayo and Lewis [3] (Table 1).

TABLE 1. Copolymerization Constants r_1 and r_2 for 1-Vinyl-2-pyrrolidinone, Methyl Methacrylate, and Acrylonitrile

Monomer	r_1	Monomer	r_2
Methyl methacrylate	1.3 ± 0.02	1-Vinyl-2-pyrrolidinone	0.16 ± 0.02
Acrylonitrile	0.74 ± 0.02	1-Vinyl-2-pyrrolidinone	0.84 ± 0.02

After the experimental part of this investigation had been completed a paper appeared which gave the copolymerization constants for methyl methacrylate (r_1) and 1-vinyl-2-pyrrolidinone (r_2): $r_1 = 4.7$ and $r_2 = 0.005$ [4]. However, it does not appear to be possible to verify these constants because the physical properties of the original vinylpyrrolidinone are not stated. Moreover, The Kjeldahl method is used in the analysis of the copolymers, and this has been shown to give low results for nitrogen in such compounds.

Table 2 gives comparative data on the activities of the monomers studied and their radicals. If it is assumed that the rate constant for the reaction of the vinylpyrrolidinone radical with its monomer is unity (on the assumption that the rate constant does not depend on the medium), then we obtain a series of values representing the relative activities of the monomers studied with respect to a common radical of the vinylpyrrolidinone type.

Table 2 shows that, with respect to the vinylpyrrolidone raidcal, the most active monomer is methyl methacrylate.

TABLE 2. Relative Activities of Monomers (1/r) with Respect to Radicals

Monomer	Radical		
	vinylpyrrolidinone	methyl methacrylate	acrylonitrile
Vinylpyrrolidinone	1.0	0.8	1.3
Methyl methacrylate	6.0	1.0	7.0
Acrylonitrile	1.2	0.8	1.0

TABLE 3. Copolymers of Methyl Methacrylate (MMA) and Vinylpyrrolidinone (VP)

Composition of mixture of monomers taken (moles %)		Yield of copolymers, %	Methyl methacrylate, %	Contents of monomer units in copolymer (moles %)	
MMA	VP			MMA	VP
100	–			100	–
90	10	99.0	Traces	–	–
75	25	96.8	2.74	80.0	20.0
50	50	83.0	5.06	62.4	37.6
25	75		5.7	57.4	42.6
		81.4*	8.77	32.6	67.4
10	90	85.2	9.35	27.8	72.2
–	100	72.0	12.6	–	100

* Three fractions differing in solubility were isolated.

The solubility characteristics of the copolymers were determined.

It is well known that acrylonitrile Polymers are soluble in a limited number of substances. It was of interest to determine the effect of the presence of vinylpyrrolidinone units on the solubility of copolymers containing acrylonitrile units. Solubilities were studied at room temperature and at higher temperatures. It was found that the copolymers of vinylpyrrolidinone and methyl methacrylate are soluble in acetone, ethanol, butyl alcohol, benzene, dioxane, chloroform, 2-ethoxyethanol, ethyl acetate, and butyl acetate. The copolymers of vinylpyrrolidinone and acrylonitrile are not soluble in these solvents. These copolymers dissolve in 2-pyrrolidinone, 1-vinyl-2-pyrrolidinone, 1-

butyl-2-pyrrolidinone, butyrolactone, 2-(2-oxo-1-pyrrolidinyl)ethyl formate, and 2-(2-oxo-1-pyrrolidinyl)ethyl acetate. Acrylonitrile homopolymer is insoluble in these solvents.

EXPERIMENTAL

Freshly distilled monomers were used; they had the following constants: Methyl methacrylate; b.p. 100°; n_D^{20} 1.4156; d_4^{20} 0.9360. Acrylonitrile; b.p. 77.3°; n_D^{20} 1.3910; d_4^{20} 0.806. 1-Vinyl-2-pyrrolidinone; b.p. 71–72° (2.5 mm); n_D^{20} 1.5117; d_4^{20} 1.0458. The polymerization was carried out in presence of azodiisobutyronitrile (0.2%) at 60 ± 1° for

TABLE 4. Copolymers of Acrylonitrile (AN) and Vinylpyrrolidinone (VP)

Comp. of orig. mixture of monomers (moles %)		Yield of copolymer (%)	N content of copolymer (%)	Content of monomer units in copolymer (moles %)		Monomer not entering copolymer (moles %)	
VP	MMA			VP	MMA	VP	MMA
100	—	52,0	26,4	100			
90	10	62,0	20,81	75,4	24,6	59,4	40,6
75	25	80,0	18,94	64,1	35,9	46,0	54,0
50	50	71,0	16,48	44,9	55,1	28,0	72,0
25	75	57,0	15,38	35,0	65,0	20,3	79,7
10	90	52,0	12,91	3,1	96,9	1,5	98,5
—	100	72,0	12,6	—	100	—	—

100 hours. Different concentrations of monomers were taken. The copolymers obtained were repeatedly reprecipitated until there was no reaction with bromine for the presence of a double bond. The copolymers of vinylpyrrolidinone and methyl methacrylate were dissolved in acetone and precipitated with methanol; the copolymers of vinylpyrrolidinone and acrylonitrile were dissolved in N,N-dimethylformamide and precipitated with methanol. The copolymers were then dried to constant weight at 10^{-3} mm and analyzed for nitrogen content (Dumas micro method); the composition of the copolymer was calculated from the nitrogen content. The results are given in Tables 3 and 4.

TABLE 5. Experimental Data for Determination of Copolymerization Constants

Initial monomer composition (moles %)			Yield (%)	N content	Concentration of monomer (mg/mole)			
VP	MMA	AN			$[M^\circ_1]$	$[M_1]$	$[M^\circ_2]$	$[M_2]$
					MMA		VP	
80	20	—	4,0	1,61	39,0	37,3	9,0	9,6
60	40	—	7,2	2,83	29,0	26,2	18,9	18,2
40	60	—	7,0	3,26	19,0	16,4	27,9	27,1
20	80	—	10,4	5,57	9,0	6,1	37,0	34,8
					AN		VP	
80	—	20	4,0	16,57	9,43	8,37	40,54	39,2
80	—	20	4,6	16,57	9,43	8,17	40,54	39,0
60	—	40	3,2	15,94	22,64	21,9	34,23	33,1
40	—	60	3,6	16,43	39,6	17,5	26,1	14,3
20	—	80	2,4	17,65	62,26	61,3	15,32	15,2

To determine the relative activities of the radicals of the pairs of monomers studied we carried out copolymerizations at low conversions. The experimental results are given in Table 5. The solubilities of the copolymers were determined as follows. A sample of the copolymer was placed in a test tube and covered with the solvent. The system was kept in the cold for 24 hours. Samples that did not dissolve in the cold were heated for several hours and left hot for 12 hours.

SUMMARY

1. Copolymers of 1-vinyl-2-pyrrolidinone with methyl methacrylate and of 1-vinyl-2-pyrrolidinone with acrylonitrile were synthesized.

2. Determinations were made of the relative activities of the radicals of the monomers studied and of the solubilities of the copolymers in some organic compounds.

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MECHANISM OF THE OXIDATION OF CELLULOSE ETHERS AND ESTERS WITH OXYGEN

O. P. Koz'mina*

Institute of Macromolecular Compounds, Academy of Sciences, USSR
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As we and other investigators have shown, at high temperatures and under the action of light cellulose ethers and esters are oxidized by atmospheric oxygen [1-5]. The over-all rate of oxidative breakdown and the magnitude of the induction period characteristic for the reaction depend on the chemical structure of the ether or ester group. Known technical cellulose esters are more stable than the ethers. The oxidative-degradation processes of aliphatic esters proceed at a considerable rate (increasing from acetates to butyrates), beginning at only 160°; the acids from which the esters are derived are then eliminated together with acids and aldehydes containing fewer carbon atoms [4, 5]. With rise in temperature to 180-200° the thermo-oxidative breakdown of these esters becomes rapid without any induction period (Fig. 1, Curve 3).

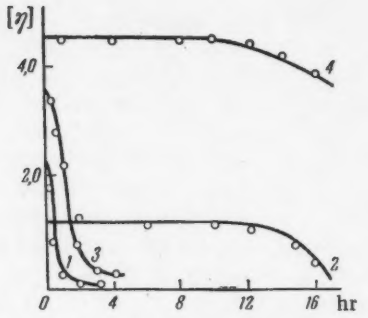


Fig. 1. Curves showing the change of the intrinsic viscosity [η] in the heating of cellulose ethers and esters in a stream of oxygen: a) triethylcellulose at 140°; 2) tritylcellulose (γ = 100); 3) cellulose triacetate; 4) cellulose tribenzoate [(2)–(4) at 180°]. In the heating of ether and ester samples in nitrogen in parallel experiments there was no change in [η] and the points lie on a straight line parallel to the axis of abscissae.

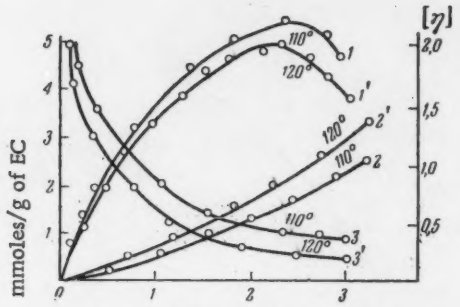
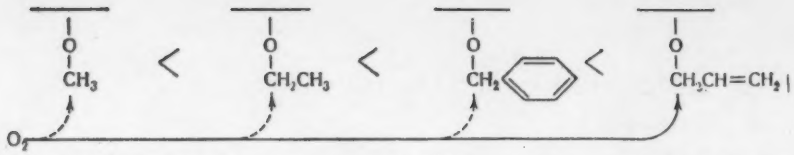


Fig. 2. Kinetics of the oxidation of ethylcellulose (EC): 1) and 1') accumulation of ethylcellulose peroxides at 110° and 120°; 2) and 2') the same for carboxy groups; 3) and 3') lowering of the intrinsic viscosity of EC at 110° and 120°.

The esters of aromatic acids are more stable than those of a aliphatic acids. Thus, the ester linkage in cellulose benzoates is not broken down in prolonged heating of the ester at 180°, or even at 200°; under these conditions, however, the degree of polymerization of the benzoate slowly falls (Fig. 1, Curve 4).

Cellulose ethers are especially prone to oxidative degradation. The rate of oxidation is determined by the mobility of the hydrogen atom at the ether carbon atom, and it increases along the series

* The work was carried out in collaboration with V. I. Kurlyankina, M. K. Aleksandrovich, É. P. Prosviryakova, P. A. Slavetskaya, and M. P. Kozlov.



The activating effect of a double bond adjacent to the ether carbon is so great that allylcellulose oxidizes already at ordinary temperatures without a period of induction. On the other hand, the ethers of tertiary alcohols, in which there is no mobile hydrogen in the alkyl groups, as e.g., tritylcellulose, have enhanced stability (Fig. 1, Curve 2).

The stability of ethers and esters to oxidation depends also on their physical properties, in particular on the phase state, which determines the rate of diffusion of oxygen into the macromolecule and therefore also the rate of oxidation. It is known, for example, that crystalline polymers are more thermostable than amorphous ones. The high stability of cellulose benzoates to oxidation is probably due to not only the chemical nature of the ester group, but to the crystallinity of the polymer [6] and the high temperatures of the transition to the highly elastic state (155-168° for various samples).

Impurities in technical samples of cellulose ethers and esters will, depending on their nature, accelerate or retard oxidative degradation. Hence, in estimates of stability to oxidation the nature of the impurities must be taken into account. Thus, technical samples of cellulose ethers and esters have different stabilities to oxidation depending on the nature of metal salt and hydroxide impurities [5, 7]. Cellulose ethers and esters containing small amounts of metallic impurities may be oxidized in different ways. As we have shown, this depends on the conditions and duration of the preliminary storage of the ethers or esters: oxidation proceeds even at ordinary temperatures, and peroxides and volatile decomposition products accumulate in the cellulose derivative, so that the oxidation of samples that have been kept for a long time at elevated temperatures is more rapid [4, 5, 7, 8]. To reestablish the induction periods it is necessary first to destroy the peroxides and remove low-molecular-weight impurities.

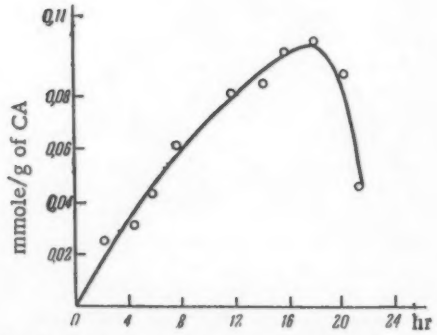
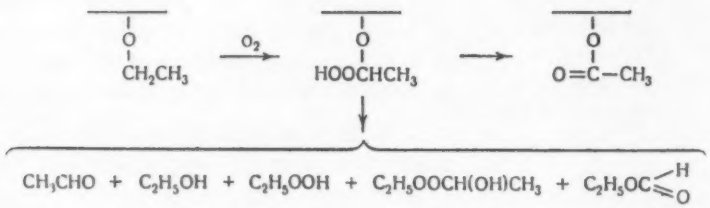


Fig. 3. Kinetics of the accumulation of peroxides in the photooxidation of cellulose triacetate (CA) (ultraviolet source: PRK-2 lamp; 50°).

Study of the chemistry and kinetics of the oxidation reaction shows [7-9] that the reaction proceeds through the stage of the formation and breakdown of ether or ester peroxides (Figs. 2-4). Curves for the accumulation of peroxides having a characteristic maximum are found when the ether or ester, e.g., ethylcellulose, is readily oxidized at medium temperatures (70-120°). With rise in temperature the peroxides are mainly decomposed at the moment of formation. Hence, in the thermo-oxidative degradation of esters (160°) no appreciable accumulation of peroxides could be observed. If the oxidation is carried out with ultraviolet irradiation at ordinary or slightly elevated temperatures, then maxima are observed for esters also (Fig. 3).

In the oxidation of cellulose ethers the action of the oxygen is directed on the alkyl groups, which is definitely proved by the investigation of the secondary oxidation products, e.g., aldehydes, alcohols, alkyl peroxy compounds, and ester groups in the macromolecules of the ethers (1):



All these products were identified [9-11] and their formation from alkyl groups proved by the oxidation of specially prepared radioactive ethers and esters [12] labeled with C^{14} in the alkyl groups. The compositions of the

alkyl hydroperoxides and peroxides were proved by chemical analysis and characteristic properties and reactions and also by he polarographic method. As well as alkyl-containing products (Fig. 4) there were formed: water, hydrogen,

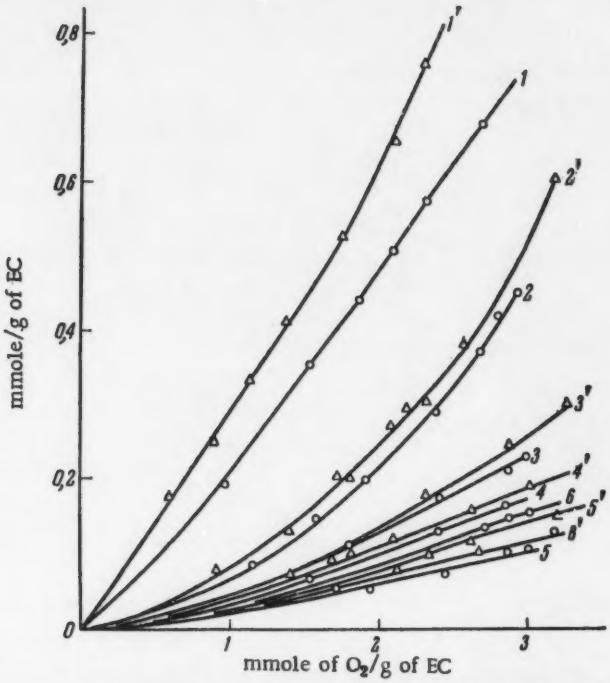


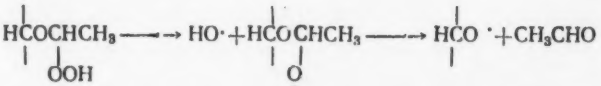
Fig. 4. Kinetics of the accumulation of volatile products in the oxidation of ethylcellulose (EC) at 110° (o) and 120° (Δ): 1) and 1') acetaldehyde; 2) and 2') formic acid; 3) and 3') alkyl peroxy compounds; 4) and 4') ethanol; 5) and 5') ethyl formate; 6) and 6') CO_2.

formic acid, carbon dioxide, and carbon monoxide. By the method of labeled atoms [12] we succeeded in showing that the last three arise mainly not from alkyl groups, but from the glucose unit.

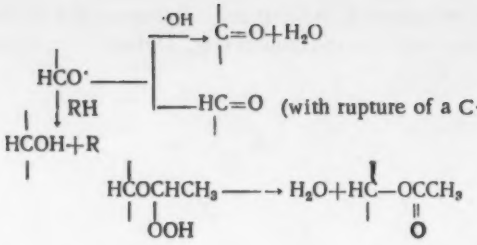
In the ethylcellulose macromolecule carboxy groups accumulate as it is progressively oxidized (Fig. 2, Curves 2 and 2'); there is an increase also in the number of carbonyl and ester groups, and the content of alkyl groups falls [9, 10] in correspondence with the amount of their oxidation products formed. It will be seen from Figures 2 and 4 that, as we pass from 110° to 120°, the character of the oxidation of ethylcellulose does not change, but there is merely an increase in the rate of the breakdown of ethylcellulose peroxides and in the accumulation of secondary reaction products.

With lowering of the temperature there is fall in the over-all rate of the oxidation, but the composition of the products formed in the range 70-130° changes only slightly, except in respect of the peroxy compounds (and the volatile and macromolecular compounds), the amount of which falls sharply with rise in temperature to 130°.

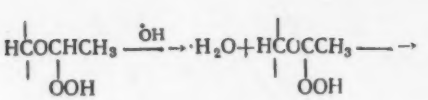
The transformations of primary peroxides of cellulose ethers and esters and of the secondary products of their breakdown (1) may be represented by the following schemes



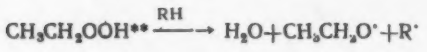
(2)



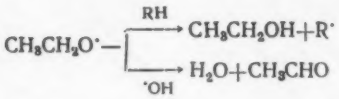
(with rupture of a C-C link in a glucoside unit) (2a)

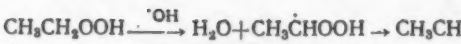


(3)

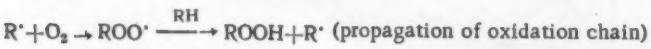


(4)



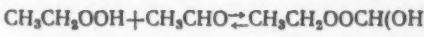


(5)

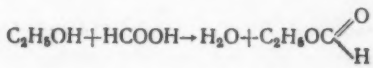


(6)

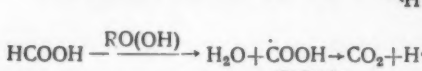
As will be seen from the schemes (2-6) there are several ways in which the products obtained in the oxidation can be formed; this is especially true of acetaldehyde and water, which are obtained in the reaction in large amounts. The formation of other low-molecular-weight compounds found may be represented by the schemes (7-9):



(7)



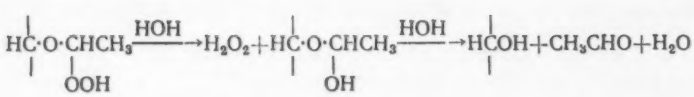
(8)



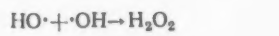
(9)

Ethyl formate, CO_2, and CO may also be formed directly in the breakdown of the oxidized glucose unit.

A leading part in the propagation of the chain radical process is undoubtedly played by hydroxyl radicals arising from low-molecular-weight alkyl hydroperoxides and hydroperoxides of cellulose ether and esters (ROOH), and also from hydrogen peroxide, which, though not detected in the final reaction products, may be formed in accordance with schemes (10), (11), and (13):



(10)



(11)

*RH = ethylcellulose, formic acid, ethyl formate, hydroperoxides, etc.

**Ethyl hydroperoxide may be formed in the oxidation of ethyl radicals, which probably arise in the system or otherwise.

$$RH+O_2 \rightarrow HO_2^{\cdot}+R^{\cdot} \quad (12)$$

$$HO_2+RH \rightarrow H_2O_2+R^{\cdot} \quad (13)$$

As it is formed, it reacts. HO_2 is a radical participating in the propagation of the chain oxidation process, which is not limited to the possible scheme (13).

It is quite probable also that the volatile aldehydes act catalytically, as has been proved [13] for the oxidation of hydrocarbons. In fact, on addition of acetaldehyde at the start of the oxidation of ethylcellulose the reaction is accelerated, but products of the oxidation of the aldehyde have not been found experimentally in any appreciable amount. It is probable that the oxidation of aldehydes in the propagating process is suppressed by formic acid, and also by their condensation with hydroperoxides as hydroxy alkyl peroxides [Reaction (7)].

The autocatalysis of the heterogeneous process of the oxygen oxidation of cellulose ethers in the solid or highly elastic state is most probably effected by low-molecular-weight oxidation products, which penetrate and attack the sluggish macromolecules of the cellulose derivatives.

For all the cellulose ethers that we have investigated, the oxidation processes are analogous to that considered for the case of ethylcellulose. There are, however, peculiarities arising from the different chemical structures of the substituents. Thus, in the oxidation of unsaturated ethers, not only peroxy, carbonyl, and other oxidized groups are formed, but also epoxy groups, and the cross-linking of the macromolecular chains of the ethers occurs. The epoxy groups probably arise by the action of low-molecular-weight peroxy compounds on the double bond of the ether as a result of reactions (14) and (15).

$$\left|-OCH_2CH=CH_2+O_2\rightarrow\right| -OCHCH=CH_2- \left|\begin{array}{l} \xrightarrow{RH} CH_2=CH-CHO+R^{\cdot} \\ \quad\quad CH_2-CH=CH_2\ (?) \\ \xrightarrow{\cdot OH} OOH \quad (R'OOH)\ \text{etc.} \end{array}\right. \quad (14)$$
(OOH)

$$\left|-OCH_2CH=CH_2+R'OOH\rightarrow\right| -OCH_2CH-CH_2+R'OH(CH_2=CHCH_2OH) \quad (15)$$
(O)

Intermolecular reaction between reactive epoxy groups of the ether or between these and double bonds may explain the cross-linking of the cellulose chains. However, with a double bond in presence of free radicals a cross-linked structure may be formed also in other ways.

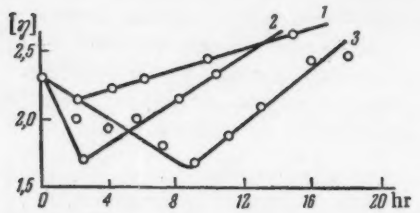


Fig. 5. Change in intrinsic viscosity in the oxidation of allylcellulose in solution: 1) at 20°; 2) at 40°; 3) at 50°.

For the oxidation of dilute solutions of allylcellulose we succeeded in demonstrating the first stage of the reaction, which is characterized by a fall in intrinsic viscosity, as in the case of saturated ethers (Fig. 5). From Figure 5 it will be seen that with rise in the temperature of the oxidation from 20° to 50° both the breakdown of the macromolecules and the start of their cross-linking are speeded up (the fall in the curve is greater and the curve is displaced to the left). With further rise in temperature the curves level out; a lowering in viscosity is no longer observed: only a smooth rise is observed. The oxidation of ethylcellulose in solution under analogous conditions proceeds at a low rate, and its intrinsic viscosity falls continuously.

The schemes proposed (1-15) do not exhaust all the possible reactions of the numerous final and intermediate oxidation products, but they are the most probable and they satisfactorily explain the formation of the compounds found experimentally.

Analogous schemes for the oxidation of ethylcellulose were proposed by McBurney [2], but in a more detailed study of the process we succeeded in discovering new reaction products, which enables one to make a more reliable assessment of the mechanism of the process. It is still not clear how the breakdown of the ether macromolecule occurs. In the oxidation of ethylcellulose radioactivity labeled (C^{14}) at C−1 of the glucose unit* we obtained about 30% of

*The radioactive cellulose used for the synthesis of ethylcellulose was prepared from the corresponding glucose by the bacterial method, and it contained 97% of labeled carbon at C−1.

formic acid, which indicates rupture of the 1,2-bond on oxidation, as envisaged in scheme (2), as a result of which cleavage of the cellulose macromolecule occurs in this position. In the oxidation of ethyl ethers of xylan (which we prepared for the first time) we again obtained formic acid in amounts similar to those obtained in the oxidation of ethylcellulose. From this it follows that formic acid is not formed from C—6 of the glucose unit, as it might be supposed to be.

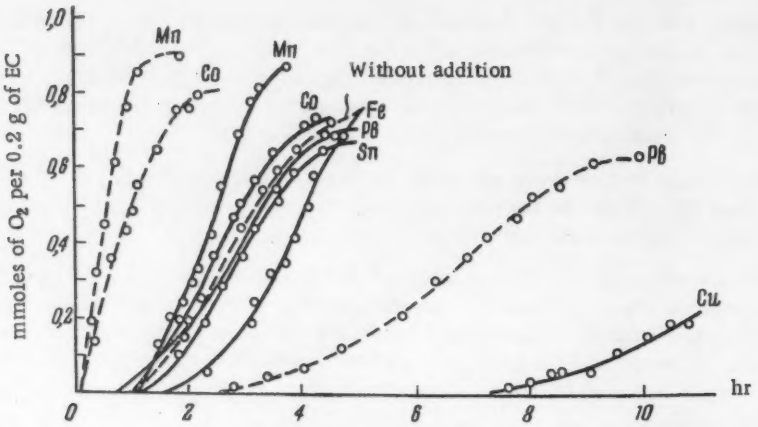


Fig. 6. Kinetic curves for the oxidation of ethylcellulose films with additions of metal naphthenates (the metals used are indicated on the corresponding curves): full curves-with addition of $2.466 \cdot 10^{-6}$ mole of naphthenate per g of EC; broken curves-with addition of $49.320 \cdot 10^{-6}$ mole of naphthenate per g of EC and without addition.

The breakdown of the macromolecules may occur in different ways simultaneously: both in coordination with the oxidation of the ether (ester) groups and by reaction of free radicals with mobile hydrogen atoms, particularly at C—1, but also and C—4 and C—5. In confirmation of the latter we may refer to the experiments described in [5] on the cleavage of ethylcellulose with methylphenyltriazene in absence of oxygen in solution at 110° (the intrinsic viscosity falls from 2.3 to 0.72 during four hours of heating*), which indicate the readiness with which the cellulose chain breaks down under the action of free radicals. Finally, under acid conditions, in addition to oxidative breakdown, it is possible also to have hydrolytic breakdown of the macromolecule at the glucosidic linkages.

The oxidative breakdown of cellulose ethers and esters is retarded by additions of inhibitors, including phenol- and amine-formaldehyde, epoxy, and other resins, lignin etc., and also metal salts and hydroxides [5, 7, 8]. Our experiments have shown that copper, iron, and also tin and lead salts inhibit the oxidation of cellulose ethers, whereas cobalt and manganese salts accelerate the oxidation (Fig. 6). These differences in the action of salts of metals of variable valence may be associated with the oxidation-reduction potentials of the metals. The oxidation of cellulose ethers and esters is also retarded by salts and hydroxides of alkali and alkaline-earth metals, probably because of the decomposition of hydroperoxides or their binding as salts, which leads to termination of the oxidation chains.

SUMMARY

1. The oxidative degradation of cellulose ethers and esters proceeds through the stage of the formation and breakdown of peroxy compounds.

2. The formation of hydroperoxides as primary and secondary reaction products and also of other compounds that readily generate free radicals, clearly marked periods of induction characteristic for autocatalytic processes, the acceleration and retardation of the process by additions of promotors and inhibitors of oxidation: all these indicate that the oxidation of cellulose ethers and esters by molecular oxygen proceeds by a chain radical mechanism.

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* Analogous results are obtained in the action of peroxy compounds, quinones, and other radical-forming substances (hydrogen acceptors) on cellulose ethers and esters.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

SHORT COMMUNICATIONS

MICRODETERMINATION OF METHOXY AND ETHOXY GROUPS

V. A. Klimova and K. S. Zabrodina

N. D. Zelinskii Institute of Organic Chemistry of the Academy of Sciences of the USSR

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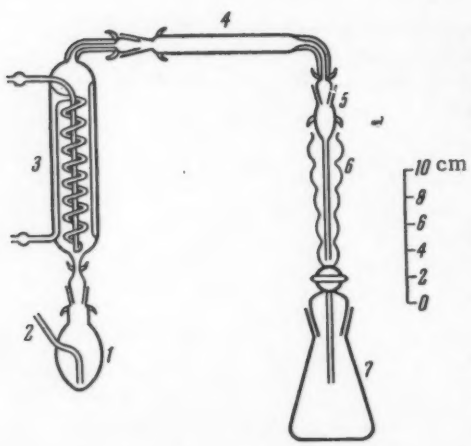
Original article submitted May 29, 1961

The microdetermination of alkoxy groups is generally carried out by Zeisel's method [1], as modified by Viebock [2]. The method is based on the decomposition of the substance to be analyzed by concentration hydriodic acid (sp.g. 1.7-1.96) with the formation of the alkyl iodide. Commercial hydriodic acid does not always satisfy the appropriate requirements; in addition, on storage it readily decomposes liberating free iodine. In consequence of this, the analyst is compelled to spend much time on the preparation of concentrated hydriodic acid and its purification. In the microdetermination of alkoxy groups, in place of hydriodic acid we have used a mixture of potassium iodide and orthophosphoric acid, the heating of which yields hydriodic acid.

EXPERIMENTAL



Apparatus for the determination: 1) reaction flask; 2) nitrogen feed tube; 3) condenser; 4) tube containing ascarite; 5) gas-discharging tube; 6) receiver; 7) conical flask.

The determination was carried out in the apparatus shown in the figure. To purify the alkyl iodide distilling over, a tube containing ascarite [3] was used, a layer of it (length ~ 9 cm) being placed between two layers of glass wool. Nitrogen was supplied from a gasometer; the rate of flow of the nitrogen was measured with a flowmeter.

The following were used as reagents: potassium iodide, orthophosphoric acid (sp.gr. 1.70), phenol, 20% aqueous sodium acetate, 2% formic acid, 10% sulfuric acid, 0.02 N sodium thiosulfate solutions, and 0.5% starch solution.

The absorption solution is prepared in the following way: 20 g of sodium acetate (trihydrate) is dissolved in 200 ml of 98% acetic acid and 1 ml of iodine-free bromine is added.

After previously wetting the joints with water, the upper end of the condenser is connected with the ascarite tube which, in its turn, is connected with the gas discharge tube. A sample of solid substance (2-6 mg) is transferred by difference from a weighing tube into the reaction flask and 0.1 g of phenol was added to it. If the material has a high boiling point, the mixture is heated to complete solution. Then 1.2 g of potassium iodide and 2 ml of orthophosphoric acid are added to the cooled solution.

In the case of non-volatile liquids, sample is weighed in a thin-walled glass tube and dropped into the reaction flask in which 0.1 g of phenol, 1.2 g of potassium iodide, and 2 ml of orthophosphoric acid have previously been placed. The tube is broken with a glass rod, which is left in the flask. The reaction flask is connected with the condenser, through which water is passed, the joint being moistened with orthophosphoric acid. Then the gas-discharge tube is lowered to the bottom of the receiver, into which 6 ml of the absorption solution is poured. The reaction flask is heated in an air bath at 195-200° for an hour, a current of nitrogen being passed through it simultaneously at the rate of 14-15 ml/min. The heating is terminated, the contents of the receiver are run into the conical flask (capacity ~ 150 ml), into which 10 ml of 20% sodium acetate solution has previously been poured. The receiver is rinsed out twice with water (~ 10 ml), which is also run into the conical flask. To remove the excess of free bromine, 1.8 ml of

Substance	Weight of sample, mg	Alkoxy group, %		
		calculated	found	difference
Methyl ester of nitrocinnamic acid	4.468	14.98	15.06	+0.08
The same	5.780	14.98	14.92	−0.06
3-(p-Methoxyphenyl)-2-cyclohexene-1-one	4.976	15.34	15.35	+0.01
The same	5.028	15.34	15.12	−0.22
Dimethyl phthalate	2.482	31.96	31.76	−0.20
The same	2.644	31.96	31.72	−0.24
Veratrole	1.820	44.92	44.79	−0.13
The same	2.273	44.92	44.65	−0.27
Diethyl ester of succinic acid	1.828	51.74	51.46	−0.28
The same	1.934	51.74	51.49	−0.25
Ethyl ester of β-ethoxycrotonic acid	2.247	56.97	56.67	−0.30
The same	2.265	56.97	56.68	−0.29

2% formic acid is added [4]; the flask is closed with a ground-in stopper, the solution is swirled round and allowed to stand for 5 minutes. Then 5 ml of 10% sulfuric acid and 0.1 g of potassium iodide are added; the flask is closed again with the stopper, swirled until the potassium iodide has dissolved and left in the dark for 10 min. The liberated iodine is titrated with 0.02 N sodium thiosulfate, 2 ml of 0.5% starch solution being added towards the end of the titration. Results of determinations are given in the Table.

SUMMARY

In the determination of alkoxy groups, hydriodic acid may be replaced by a mixture of potassium iodide and orthophosphoric acid.

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THE REDUCTION OF CeO_2 IN THE KETONIZATION OF CH_3COOH

A. M. Rubinshtein, A. A. Slinkin, V. I. Yakerson

and E. A. Fedorovskaya

The N. D. Zelinskii Institute of Organic Chemistry of the Academy of Sciences of the USSR

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In studying the kinetics of the vapor-phase catalytic ketonization of CH_3COOH over oxides of tetravalent metals, it was shown [1] that CeO_2 possesses the highest specific catalytic activity. However, in the process of ketonization the CeO_2 itself undergoes a change which proceeds simultaneously with the decomposition of the CH_3COOH. Two samples of CeO_2 were studied. Sample A was obtained by moulding commercial CeO_2 (grade "pure"). Sample B was obtained by precipitation from a solution of $Ce(NO_3)_3 \cdot 6H_2O$ in an atmosphere of ammonia. Before the experiment, the catalysts were crushed into granules with dimensions of 1.5 × 1.5 mm. The bulk densities were 2.1 g/cm^3 (A) and 1.3 g/cm^3 (B). The method of carrying out the experiments on ketonization in a continuous system and the x-ray phase analysis of the catalysts has been described in paper [2]. The experimental results are given in Tables 1 and 2. In each experiment, a fresh portion (1 cm^3) of catalyst was used. A succession of experiments with a single portion of catalyst is indicated in Table 2 by figures in brackets. Measurement of the magnetic susceptibility of the catalysts was carried

TABLE 1. Decomposition of CH_3COOH on CeO_2 (sample A)

Temp. °C	m, ml/min.	$m_{sp.}$, ml/min/g CeO_2	Working time, min	$\chi \cdot 10^6$	Temp. °C	m, ml/min	$m_{sp.}$, ml/min/g CeO_2	Working time, min	$\chi \cdot 10^6$
288	1,05	0,50	160	+0,5	297	2,1	1,0	84	+1,9
290	1,35	0,64	90	+1,8	304	3,55	1,7	66	+1,4
292			277		314	6,3	3,0	64	
294	1,8	0,86	87	+2,2	320	8,0	3,8	62	
					333	16	7,6	66	+1,1

out before and after the experiments. The catalytic activity is expressed in milliliters of gas (CO_2) in 1 min. (m, ml/min) and in milliliters of gas in 1 min per 1 g of CeO_2 ($m_{sp.}$ = ml/min/g CeO_2). In experiments with sample B, after some experiments air was passed, whereupon a sharp (after 1.5-2 min) jump in the temperature (+Δt air) was observed. Before the passage of air, the color of the catalyst was black; after passing it, the original pale yellow. Measurement of the magnetic susceptibility showed the absence of ferromagnetic impurities. In addition, it is known [3] that CeO_2 and Ce^{+4} possess an intrinsic paramagnetism independent of the temperature; this fact is confirmed by our results. In the course of the experiments (Table 1 and 2) the paramagnetism rises, to the greater extent the greater time of contact with CH_3COOH. Treatment of CeO_2 (sample A) with hydrogen also leads to an increase in the paramagnetism (Table 3).

The value of χ for the initial sample A was close to χ for the initial sample B, as can be seen from Tables 1 and 2; however, during the catalytic experiments the first changed very slowly and the second extremely rapidly. The catalytic activity of sample B was considerably higher than that of sample A, but it rapidly fell in the course of time. Thus, in distinction from samples A, sample B has a very poor stability. Analysis of the gas evolved at various stages of the decomposition of the CH_3COOH showed only the presence of CO_2. In the catalyzate, in addition to undecom-

TABLE 2. Decomposition of CH_3COOH on CeO_2 (sample B)

Temperature °C Before the experiment	m, ml/min	$m_{sp.}$, ml/min/g CeO_2	$+\Delta t$, °C air	Working time in min	$\chi \cdot 10^6$	Color of the catalyst after the experiment
					+0,41	
313*				126	+4,0	Bluish black
293(1)			~200	51		Pale yellow
292(2)	1,2	0,79	234	93		Ditto
294(3)	1,0	0,77	190	90		»
304(4)	1,3	1,0	147	110		»
297(5)	0,75	0,58	188	107		»
294(6)	0,45	0,35	206	89	+0,43	»
295(1)	11—2,2	8,5—1,7		71		Bluish black
307(2)	4,2—0,9	3,2—0,7	180	105		Pale yellow
305(3)	3,1—0,6	2,4—0,5	140	105		Ditto
320(4)	4,3	3,3		102	+1,6	Bluish black
293(1)**	10,5—6,2	8,1—4,8	130	72		Pale yellow
291(2)	5,2—2,5	4,0—1,9		90	+2,5	Bluish black
295***	5,2—2,2	3,0—1,3		87	+0,94	Black

* After heating in air (200°, 6 hours) $\chi \cdot 10^6 = +1.4$.

** Catalyst previously heated in air (550°, 8 hours).

*** Catalyst previously heated in air (1000°, 8 hours).

posed CH_3COOH only acetone could be detected (test with 2,4-dinitrophenylhydrazine). The aldehyde reaction (silver mirror reaction and reaction with benzidine in acetic acid) was negative. The passage of air over the bluish black samples B restored not only the original color of the samples but also their magnetic susceptibility. X-ray diagrams of samples A and B before and after use were completely identical—only the CeO_2 phase was present. The results obtained indicate a process of oxidation-reduction between the CH_3COOH and the catalyst. Sample B, as mentioned above, was obtained in air, but without subsequent special oxidation, such as is usually carried out in the preparation of Ce^{+4} salts from Ce^{+3}. It is known [4, 5] that CeO_2 when 12% reduced does not differ x-radiographically from pure CeO_2. In the course of the ketonization reaction, the cyclic transfer of an electron [1] is partially broken and the reduction of part of the CeO_2 by CH_3COOH (possibly also by CH_3COCH_3) takes place. The Ce_2O_3 formed gives a solid solution with CeO_2. The bluish black color of the B samples after use (before the passage of air) agrees with the color of the material first obtained by Meyer [6] by the reduction of CeO_2 with hydrogen at a high temperature. It was later shown that the blue-black color is due to the formation of a solid solution of CeO_2 and Ce_2O_3 with the composition $CeO_{1.7}$ [4, 5]. After working (before the passage of air), sample B probably consists of solid solution of the same composition. The reduction of the catalyst apparently begins with the surface layers, holes appearing by reason of the withdrawal of oxygen from the lattice together with quasi-free electrons. The latter migrate to Ce^{+4}, giving Ce^{+3}. Since all cations occupy crystallographically equivalent places, the exchange of position between Ce^{+4} and Ce^{+3} can take place not by diffusion of the cations but by migration of an electron. The anionic vacancies, as is shown by the ease of oxidation with atmospheric oxygen of partially reduced samples, are extremely mobile. Hence, it follows that reduction in the bulk following reduction at the surface will take place by means of the migration of oxygen to the surface.

TABLE 3. Change of χ During Hydrogen Treatment

Temperature, °C	Time, hours	$\chi \cdot 10^6$
300	3	+0.5
300	6.5	+0.7
540	3	+1.0

SUMMARY

The decomposition of CH_3COOH on various samples of CeO_2 has been studied. The reduction of Ce^{+4} to Ce^{+3} with the simultaneous oxidation of the CH_3COOH has been detected.

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SYNTHESIS OF N-β-TRIFLUOROETHYL DERIVATIVES OF MALEIC AND CITRACONIC ACIDS

T. V. Sheremeteva, Z. V. Borisova, and V. V. Kudryavtsev

The Institute of High Molecular Weight Compounds of the Academy of Sciences of the USSR

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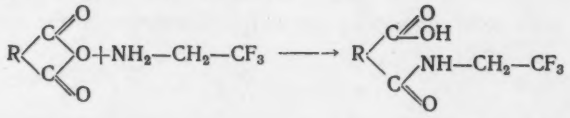
With the object of extending the investigations of our laboratory on the synthesis and study of the properties of nitrogen-containing derivatives of unsaturated dicarboxylic acids [1], the N-β-trifluoroethylamides and imides of maleic and citraconic acids, not previously described in the literature, have been synthesized.

EXPERIMENTAL PART

Synthesis of the N-β-trifluoroethylamides of maleic and citraconic acids. The synthesis was based on the interaction of the anhydrides of the acids with the corresponding amines.



The solution of the anhydride in dry benzene or chloroform was charged into a round-bottomed flask immersed in ice water and fitted with a stirrer and a reflux condenser, and a solution of the fluoramine in benzene or chloroform was added dropwise. After the addition of all the amine, the mixture was stirred for 2-2.5 hours at room temperature. The amidoacid separating in the precipitate was filtered off, recrystallized from a mixture of acetone and chloroform, and dried in a thermostat at 80°.

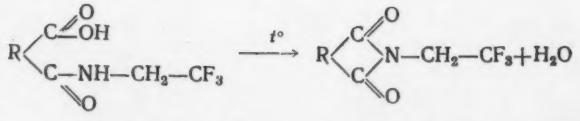
From 9.8 g (0.1 mole) of maleic anhydride and 9.9 g (0.1 mole) of β-trifluoroethylamine, a yield of 18.68 g (96%) of the N-β-trifluoroethylamide of maleic acid was obtained: m.p. 113-114°. Found: C 36.53; H 3.16; N 6.78; F 28.62%; mol.-wt. 197.4. $C_6H_6O_3NF_3$. Calculated: C 36.55; H 3.05; N 7.11; F 28.42%; mol.-wt. 197.

The N-β-trifluoroethylamide of maleic acid formed white fine crystals soluble in alcohol and acetone and insoluble in benzene, toluene, xylene, and chloroform.

From 22.5 g (0.2 mole) of citraconic anhydride and 19.8 g (0.2 mole) of β-trifluoroethylamine, a yield of 41.45 g (96.02%) of the N-β-trifluoroethylamide of citraconic acid was obtained; m.p. 139-140°. Found: C 39.74; H 3.64; N 6.58; F 27.00%; mol.-wt. 213.3. $C_7H_8O_3HF_3$. Calculated: C 38.91; H 3.79; N 6.63; F 27.02; mol.-wt. 211.

The N-β-trifluoroethylamide of citraconic acid formed white crystals, readily soluble in alcohol and acetone and insoluble in benzene, toluene, xylene, and chloroform.

Synthesis of the N-β-trifluoroethylimines of maleic and citraconic acids. The synthesis was based on the thermal cyclization of the corresponding amides.



The N-β-trifluoroethylimide of maleic acid was obtained in a Dean and Stark apparatus [2] with the object of continuously removing water from the reaction mixture. A suspension of 2.15 g (0.011 mole) of the N-β-trifluoro-

ethylamide of maleic acid in 100 ml of toluene was placed in the flask of the apparatus. The reaction mass was heated in a silicon bath at 115-120° for three hours and then the temperature of the bath was raised to 130-135° and heating was continued for a further three hours.

The water of reaction was condensed in the trap of the apparatus. The N-β-trifluoroethylimide of maleic acid formed was readily soluble in toluene but separated from the solution on cooling in solid carbon dioxide.

After recrystallization from methyl alcohol and sublimation, 0.6 g (30.6%) of the N-β-trifluoroethylimide of maleic acid was obtained: m.p. 62-63°. Found: C 40.38; H 2.24; N 7.39; F 31.98%. $C_6H_4O_2NF_3$. Calculated: C 40.23; H 2.24; N 7.82; F 31.84%.

The N-β-trifluoroethylimide of maleic acid formed white lustrous needle-shaped crystals, soluble in organic solvents.

The N-β-trifluoroethylimide of citraconic acid was obtained by heating the N-β-trifluoroethylamide of citraconic acid in an apparatus for vacuum distillation (with a thermometer immersed in the reaction mixture was maintained at 130° for 6 hours and 150° for 1 hour. Then the reaction mass was twice subjected to vacuum distillation in a current of nitrogen and was recrystallized from a mixture of petroleum ether and chloroform. From 7.75 g (0.037 mole) of the N-β-trifluoroethylamide of citraconic acid, a yield of 4.2 g (59%) of the N-β-trifluoroethylimide of citraconic acid was obtained: m.p. 42-43°. Found: C 43.68; H 3.31; N 7.32; F 28.89%. $C_7H_6O_2NF_3$. Calculated: C 43.75; H 3.12; N 7.29; F 29.01%.

The N-β-trifluoroethylimide of citraconic acid forms white sublimable crystals, readily soluble in organic solvents.

The authors express their thanks to A. G. Ashuev and A. M. Marshak for a gift of β-trifluoroethylamine and the analytical laboratory of the Institute of High Molecular Weight Compounds of the Academy of Sciences of the USSR for performing the analyses.

SUMMARY

Halogen derivatives of the N-alkylmonoamides and N-alkylimides of maleic and citraconic acid containing the strongly electronegative group CF_3 in the alkyl radical, previously unreported in the literature, have been synthesized.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

INFLUENCE OF THE STRUCTURE OF THE DOUBLE LAYER ON THE POLAROGRAPHIC BEHAVIOR OF NITRO COMPOUNDS

S. G. Mairanovskii and Ya. P. Stradyn'

The N. D. Zelinskii Institute of Organic Chemistry of the Academy of Sciences of the USSR
The Institute of Organic Synthesis of the Academy of Sciences of the Latvian SSR
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It is known that the structure of the double layer exerts a considerable influence on the value $E_{\frac{1}{2}}$ of irreversible polarographic waves. The structure of the double layer influences the effective difference in the potentials $E-\psi_1$ determining the rate of electron transfer [1,2] and also the value of pH in the peri-electrodic layer [3]. In the present paper, the influence of the structure of the double layer on $E_{\frac{1}{2}}$ of the first polarographic waves in the reduction of nitrobenzene, phenylnitromethane, and 1-nitropropane in a weakly acid medium is studied.

EXPERIMENTAL PART

The polarograms were obtained on a PE-312 recording polarograph [4] with potentiometric adjustment (accuracy ± 2.0 mv) of the potential of the dropping electrode [5]. The work was carried out in a thermostated cell [6] at 25° in an atmosphere of nitrogen. The dropping electrode (with blade) had the following characteristics: t = 0.22 sec; m = 0.73 mg/sec. An acetate buffer solution was used, the pH of the solution and its buffering capacity being maintained strictly constant in each series of experiments. In some cases, ethyl alcohol was present in the solutions (0.4 or 1.6% by weight), the concentration of the alcohol being kept constant for any one series of experiments. In the first three series of experiments, with the pH of the acetate buffer (pH 4.65), the concentration of potassium acetate in it (0.10 M), and the concentrations of the nitro compounds (0.32 mM) being kept constant, the salts KCl, CsCl, and KI were added to the solution, their concentrations varying from 0 to 1.5 M (for KCl and KI) and to 0.7 M (for CsCl). In all

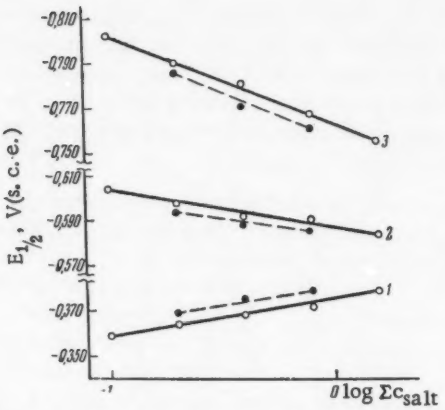

Fig. 1. $E_{\frac{1}{2}}$ of the waves of nitrobenzene (1), phenylnitromethane (2), and 1-nitropropane (3) as a function of the total salt content (0.1 N CH_2COOK + MCl) in the solution; O for KCl; ● for CsCl.

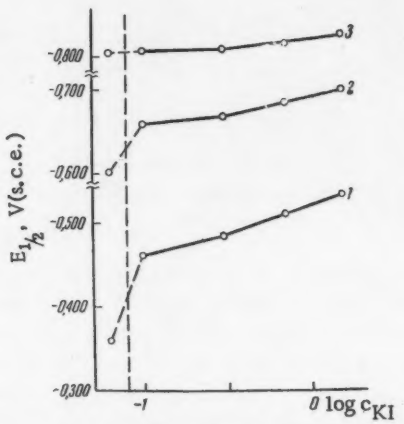

Fig. 2. $E_{\frac{1}{2}}$ of the waves of nitrobenzene (1), phenylnitromethane (2), and 1-nitropropane (3) as a function of the concentration of KI in the solution. The value of $E_{\frac{1}{2}}$ in the absence of KI is given on the left.

cases, increasing the concentration of the salt in the solution had an effect on $E_{\frac{1}{2}}$ of the waves of the compounds studied (Figs. 1 and 2). In the case of nitrobenzene, the reduction proceeded along the positive branch of the electrocapillary curve (ECC), so that Cl^- anions exerted predominating influence on the Ψ_1 potential (and consequently on $E_{\frac{1}{2}}$ also), wherefore, with a rise in the concentration of the latter, Ψ_1 becomes negative and $E_{\frac{1}{2}}$, on account of the change in the effective potential jump, must be displaced in the negative direction. The reduction of nitro compounds in an acid medium takes place with the predominating protonization of the nitro group and, if the protonization proceeds in a sufficiently thin peri-electrodic layer or— if partially—on the surface of the electrode (with the participation of adsorbed molecules), its rate must exert an influence also on the value of the pH at the electrode surface, which, in its turn, also depends on the Ψ_1 potential [1, 3, 7]. In the case of a negative Ψ_1, when it increases the absolute value of the pH in the peri-electrodic region remains low, and $E_{\frac{1}{2}}$, (on account of the change in pH) must remain postive. The displacement observed for the nitrobenzene wave $\Delta E_{\frac{1}{2}}/\Delta \log \Sigma_{salt} \approx -15$mV indicates the predominance of the first of the effect mentioned. Consequently, protonization proceeds both in the bulk of the solution and in the surface layer in this case [8].

Phenylnitromethane is reduced on the negative branch of the ECC, where cations also affect Ψ_1; therefore the value of the concentration of K^+ in the solution reduces the negative Ψ_1 potential (assuming that the point of zero charge lies at -0.45 v, on passing from 0.1 to 1.0 N KCl, Ψ_1 changes by ~25 mv), on account of which $E_{\frac{1}{2}}$ must remain positive at the same value. However, the observed displacement $\Delta E_{\frac{1}{2}}/\Delta \log c_{K^+} \approx +16$ mv is considerably less than the change in the Ψ_1 potential. This may be due to an increase in the pH in the peri-electrodic layer with the increase in c_{KCl} [3] and the displacement of $E_{\frac{1}{2}}$ to a negative potential taking place in consequence of it. The smallness of the latter effect indicates, apparently, that the protonization reaction takes place not only at the surface but also in the bulk of the solution [8]. For the wave of 1-nitropropane, the observed value of $E_{\frac{1}{2}}/\Delta \log c_{K^+} \approx +37$ mv almost agrees with the change in the Ψ_1 potential; consequently, in this case, the effect of the change of pH in the peri-electrodic layer is almost nil. This may be explained by the relatively low adsorbability of 1-nitropropane, leading to a reduction in the surface protonization reaction [8].

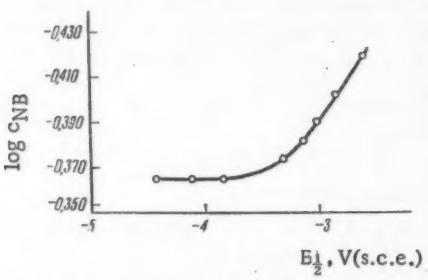

Fig. 3. $E_{\frac{1}{2}}$ of the nitrobenzene wave as a function of its concentration in the solution.

As can be seen from the data of Figure 1, replacement of KCl by CsCl leads to a slight effect, which was to have been expected for potentials close to the electrocapillary zero [9]. However, replacement of the anion Cl^- by I^- leads to a sharp displacement of $E_{\frac{1}{2}}$ to negative potentials (Fig. 2). This effect is connected with the adsorption of the I^- ions, leading to a diminution in the Ψ_1 potential [2]. The greatest displacement of $E_{\frac{1}{2}}$ is observed in the case of nitrobenzene, apparently as positive as those at which nitrobenzene is reduced. With an increase in the cathode potential, the adsorbability of I^- falls, and simultaneously the opposite action of K^+ begins to be exerted on Ψ_1; therefore on passing to the wave of phenylnitromethane and on to that of 1-nitropropane, the influence of the I^- ions diminishes (Fig. 2).

It is possible to explain the displacement of $E_{\frac{1}{2}}$ frequently observed with the concentration of the nitro compound in the solution by a change in the structure of the double layer caused by the adsorbed product of the electrode reaction—the corresponding hydroxylamine [10-12]. Figure 3 gives the dependence of $E_{\frac{1}{2}}$ on the concentration of nitrobenzene in an acetate buffer solution with pH 4.80 and with a sufficiently high buffering capacity ($C_{CH_3COOH} \approx 0.1$ N) which we observed. At a low concentration of nitrobenzene, when the coating of the surface with the electrode products is small, particularly with the short-period electrode which we used, $E_{\frac{1}{2}}$ does not depend on the concentration of the depolarizer. The influence of the concentration on the $E_{\frac{1}{2}}$ of nitrobenzene (NB) begins to be exerted, in our case, only at $C_{NB} \approx 2.5 \cdot 10^{-4}$ M. For the 1-nitropropane wave, when the adsorbability of propylhydroxylamine is lower than that of phenylhydroxylamine, according to our experiments a concentration of depolarizer $\leq 5 \cdot 10^{-3}$ M has practically no influence on $E_{\frac{1}{2}}$. When capillaries with a greater dropping period are used, with an increase in the concentration of nitromethane $E_{\frac{1}{2}}$ is displaced to positive potentials [12], which is due to the adsorption of cations of methylhydroxylamine, diminishing the negative Ψ_1 potential.

SUMMARY

The structure of the double electrical layer has a considerable effect on the half-wave potential of the logarithmic wave of the reduction of nitrocompounds, the change in the effective potential jump exerting the main influence; the increase in the pH in the peri-electrodic layer on increasing the ionic strength of the solution has a considerably smaller effect.

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KINETICS OF THE DECOMPOSITION OF SYMMETRICAL ORGANOMERCURY COMPOUNDS

A. N. Nesmeyanov, A. E. Borisov, and I. S. Savel'eva

Institute of Heteroorganic Compounds of the Academy of Sciences of the USSR
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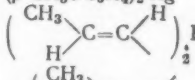
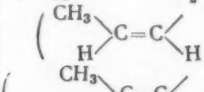
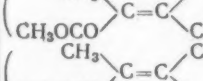
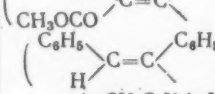
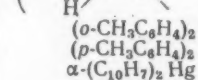
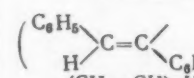
In one of the previous communications [1] we reported a series of constants for the rate of acidolysis of symmetrical organomercury compounds according to the scheme

$$R_2Hg + HCl \rightarrow RHgCl + RH$$

Velocity Constants for the Decomposition of Symmetrical Organomercury Compounds by Hydrogen Chloride in Different Solvents (l /M/sec). The constants relate to 30°, with the exception of those denoted with asterisks, the temperature of which are given in footnotes.

No. in order of decreasing constant in tetrahydrofurane	Formula	In tetrahydrofurane		In dioxane		In order of decreasing constant in dioxane
		At a ratio of 9.64: 0.36	Yield %	At a ratio of 9:1	At a ratio of 9.64: 0.36	
1	2	3	4	5	6	7
1	$(C_6H_5CH=CH)_2Hg$	1,09	84,4	$9,11\cdot10^{-2}$*	1,09*	4
2	$(p\text{-}CH_3OC_6H_4)_2Hg$	$9,42\cdot10^{-1}$	79	$1,15\cdot10^{-1}$*	1,44*	3
3		$8,07\cdot10^{-1}$	84	$2,21\cdot10^{-1}$*		1
4		$6,68\cdot10^{-1}$	79	$1,75\cdot10^{-1}$*	2,23*	2
5		$4,91\cdot10^{-1}$	71,4	$5,48\cdot10^{-2}$*	$7,13\cdot10^{-1}$*	5
6		$3,14\cdot10^{-1}$	85,8	$4,60\cdot10^{-2}$*	$5,12\cdot10^{-2}$*	6
7		$1,29\cdot10^{-1}$	94	$2,36\cdot10^{-2}$		9
8	$(o\text{-}CH_3C_6H_4)_2Hg$	$9,98\cdot10^{-2}$	77	$4,5\cdot10^{-2}$	$1,28\cdot10^{-1}$*	7
9	$(p\text{-}CH_3C_6H_4)_2Hg$	$8,51\cdot10^{-2}$	85	$4,18\cdot10^{-2}$	$1,04\cdot10^{-1}$*	8
10	$\alpha\text{-}(C_{10}H_7)_2Hg$	$3,71\cdot10^{-2}$	73,2	$1,37\cdot10^{-2}$		11
11	$(m\text{-}CH_3C_6H_4)_2Hg$	$2,86\cdot10^{-2}$	65,6	$1,22\cdot10^{-2}$		12
12	$(o\text{-}CH_3OC_6H_4)_2Hg$	$2,54\cdot10^{-2}$	62	$1,53\cdot10^{-2}$		10
13	$(C_6H_5)_2Hg$	$1,77\cdot10^{-2}$	62,6	$2,36\cdot10^{-2}$** $6,65\cdot10^{-3}$		14
14		$1,55\cdot10^{-2}$	54	$1,29\cdot10^{-2}$**		15
15	$(CH_2=CH)_2Hg$	$1,43\cdot10^{-2}$	65	$8,87\cdot10^{-3}$		13
16	$(p\text{-}FC_6H_4)_2Hg$	$1,09\cdot10^{-2}$	50	$5,82\cdot10^{-3}$		16
17***	$(p\text{-}CH_3C_6H_4)_2Hg$	$6,13\cdot10^{-5}$	55			

* Constants measured at 20°.

** Constants measured at 40°.

*** The experiment was carried out in a solution of tetrahydrofurane and water in a ratio of (9:1).

A further study of this reaction by a similar method in a mixture of dioxane and tetrahydrofurane with water has made it possible for us to report the velocity constants for the decomposition of symmetrical organomercury compounds and to arrange the radicals in a sequence according to their rate of breaking away from the mercury atom with hydrogen chloride.

It follows from the velocity constants for this reaction given in the table that the rate of decomposition in dioxane with water at ratios of (9 : 1)* and (9.64 : 0.36) falls with an increase in the amount of water (compare the constants in columns 5 and 6). The same phenomenon is also observed with di-p-tolylmercury in tetrahydrofurane solution (see 9 and 17). The decomposition reaction proceeds faster in dioxane solution than in tetrahydrofurane (see 1-9). Comparison of the constants arranged in the order of decreasing reaction velocity in dioxane and in tetrahydrofurane shows that this order is, in the main, preserved, with the exception of examples (3,4,9,10, and 13 column 7). The disturbance of the order of the constants is apparently connected with the difference in polarity of the solvents.

The velocity constants were calculated from the formula for a second order reaction (deviation not greater than ± 4% on repeated determinations)

$$K = \frac{2,3}{(a-b)\tau} \lg \frac{b(a-x)}{a(b-x)}$$

where a is the concentration of hydrochloric acid; and b is the concentration of R_2Hg. At a ratio of dioxane or tetrahydrofurane to water of (9.64 : 0.36), $a \approx 0.36 \cdot 10^{-2}$ M/l, $b \approx 0.3 \cdot 10^{-2}$ M/l. At a ratio of 9 : 1, $a \approx 1 \cdot 10^{-2}$ M/l, $b \approx 0.5 \cdot 10^{-2}$ M/l.

SUMMARY

A series of organic radicals arranged in order of their rates of removal from symmetrical organomercury compounds with hydrogen chloride in different solvents is given.

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* The solvent (9 : 1) contains 90% of dioxane and 10% of water; the solvent (9.64 : 0.36) contains 96.4% of tetrahydrofurane or dioxane and 3.6% of water.

CHROMATOGRAPHIC ISOLATION OF MENTHOL

E. I. Klabunovskii, A. A. Balandin, and L. F. Godunova

The N. D. Zelinskii Institute of Organic Chemistry of the Academy of Sciences of the USSR

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The isolation of menthol from mixtures containing both the products of its catalytic conversion (menthene, menthone) and foreign compounds (ethereal oils) is of considerable interest for practical workers. The isolation of racemic menthol from the products of the catalytic hydrogenation of thymol and its purification form one of the main difficulties of the industrial production of menthol [1]. It is impossible to consider the long-used methods for the isolation of levo-menthol from peppermint oil via the boric ester and via the acetate as satisfactory [2,3]. Chromatographic methods have recently been proposed for the isolation of menthol from mixtures. However, the absence of a dependable method of analysis has made the quantitative determination of menthol difficult. Menthone and menthol have been separated quantitatively by chromatography on SiO_2 (elution with petroleum ether). By using chloroform, menthol has successfully been separated quantitatively from peppermint oil [5].

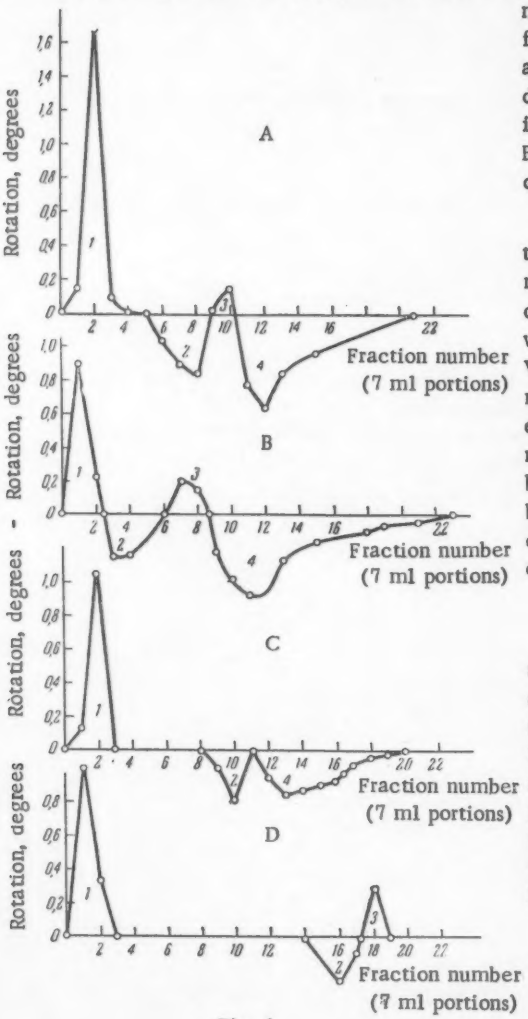

Fig. 1

In the present work, the chromatographic separation of a ternary mixture of optically active menthene, menthone, and menthol, with polarimetric analysis of the fractions was carried out. Polarimetry is being ever more widely used in conjunction with chromatography for the analysis of many organic compounds. Vavon [6] analysed a mixture of menthol and neomenthol by this method. The possibility of analysing a mixture of isomeric terpenes and menthols by the gas-liquid chromatographic method has recently been shown [7]. In such a method of analysis, the possibility of the racemization of the compound being separated must be taken into account [8]; hence, to obtain optically pure components in preparative amounts, it is advantageous to use adsorption chromatography.

EXPERIMENTAL PART

We have investigated the conditions for the chromatographic separation of a synthetic ternary mixture of menthol, menthone, and menthene. Meth-3-ene was obtained by dehydrating levomenthol with boric acid [9]: b.p. 62-63° (15-16 mm); n_D^{20} = 1.4529; d_4^{20} 0.8077; $[\alpha]_D^{20}$ +53.4° (α_D^{20} 82.04; l 1.9009). The menthone, obtained by the oxidation of menthol with chromic mixture and subjected to inversion in the course of time had b.p. 96-97° (20 mm); n_D^{20} 1.4537; $[\alpha]_D^{20}$ -2.71° (α_D^{20} 0.124, alcohol). The menthol had $[\alpha]_D^{20}$ -50.06° (alcohol); $[\alpha]_D^{20}$ -48.5 (c = 2.636, heptane).

Alumina and silica gel were investigated as adsorbents. Alumina did not give satisfactory results. Silica gel proved to be a suitable adsorbent. The following silica gels were used (160-220 mesh fractions). Silica gel 1, type "KSK" without additional treat-

ment. A stereospecific [10] silica gel 2 was obtained from waterglass (d 1.40, ratio 3.14) by the action of glacial acetic acid containing 3% of dextro-tartaric acid at 5°, pH 5. Silica gel 3 was obtained in a similar manner to silica gel 2, but in the presence of racemic acid. The reference material, silica gel 4, was obtained under the same conditions as silica gels 2 and 3, but without the addition of a forming agent. Silica gels, 2, 3, and 4 were dried a current of air with a moisture content of 60% to a moisture content of 50% and were extracted with methanol to a mixture content of 20%

The use of these silica gels was based on the data of Curti and Colombo [10], who obtained a silica gel specific for mandelic acid by forming it in the presence of camphor sulfonic acid. It was assumed that in our case the silica gel formed in the presence of tartaric acid would adsorb the hydroxyl-containing compound—menthol—more strongly. The chromatographic separation was carried out on a column (210 mm long, 12 mm in diameter) previously filled with a suspension of the adsorbent in n-heptane. Elution was performed with a mixture of heptane + 0.5% by vol. of cyclohexanone. The rate of flow was from 0.1 to 0.45 ml/min. The fractions obtained (5 ml each) were investigated polarimetrically. The results obtained are given in the figure as rotation observed (α_{obs}) against fraction number.

Curve A represents the separation of the mixture on silica gel 1. The quantitative content of menthene (peak 1) was determined bromometrically. Peaks 2 and 3 correspond respectively to menthone (2,4-dinitrophenylhydrazone, m.p. 144.5-145°) and isomenthone (2,4-dinitrophenylhydrazone, formed as a result of the inversion of the menthone [11]. The hydrazones of menthone and isomenthone were separated from the 2,4-dinitrophenylhydrazone of the cyclohexanone used as an additive to the eluent by chromatography on Al_2O_3 (eluate: n-heptane + 3% by vol. of $CHCl_3$). It was established by special experiments that the inversion of menthone did not take place in the presence of silica gel. Peak 4 belongs to menthol (color reaction with p-dimethylaminobenzaldehyde, used also for the colorimetric determination of menthol) [5] (in a FEK-M photoelectric colorimeter).

The determination of the content of the components in the chromotograph from the areas of the peaks showed satisfactory agreement with the composition of the initial mixture. The relative percentage contents of menthene, menthone, and menthol in the initial mixture and found for silica gel 1 (curve A) were equal respectively to: 29 : 31; 34 : 30; 37 : 39. The ratio of menthone to isomenthone found was 15 : 1. Curve D (separation of the mixture on silica gel 2) and curve C (separation on silica gel 3) are of particular interest. As can be seen from the curves, in spite of the strict observance of the conditions of separation, the introduction of a forming agent during the precipitation of the silica gel substantially increases its stereospecific properties (increases the separation between the peaks). The reference silica gel 4 does not possess similar stereospecificity (curve B) and does not differ from silica gel 1. The behavior of silica gel 2, formed in the presence of dextro-tartaric acid must be particularly noted: menthol proves to be so strongly adsorbed that methanol was used for its elution. The ratio of the distances between peaks 1 and 2, 2 and 3, and 3 and 4 on the graphs may be used as a measure of the stereospecificity of the silica gel. These values for curves A and B are similar and are equal respectively to 1.5 : 1 : 3. For curve D these ratios are 7 : 1 : 20. Hence, it can be seen that menthol is adsorbed on the stereospecific silica gel 2 more strongly than on silica gels 1, 3, and 4.

The polarimetric analysis for the chromatographic separation of menthol from mixtures which we have used may be proposed also for the separation of racemic menthol, if levo-menthol is added to it as an indicator. On the other hand, chromatography of similar mixtures may be used as an indicator of the stereospecificity of natural and synthetic adsorbents.

SUMMARY

1. A mixture of menthene, menthone, and menthol has been separated into its components by the method of adsorption chromatography.

2. The stereospecific action of silica gel formed in the presence of dextro-tartaric acid has been shown.

3. The method for the separation of a ternary mixture of optically active components which has been developed may be used for the determination of the stereospecificity of adsorbents.

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THE ACTION OF BUTYLLITHIUM AND BUTYLMAGNESIUM BROMIDE ON TRANS-EPOXYCYCLODODECANE

L. I. Zakharkin

The Institute of Heteroorganic Compounds of the Academy of Sciences of the USSR

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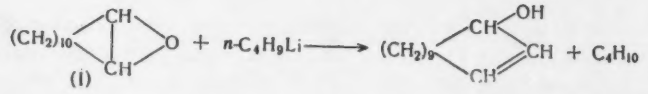
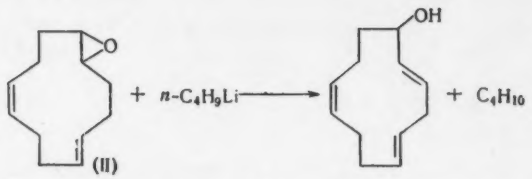
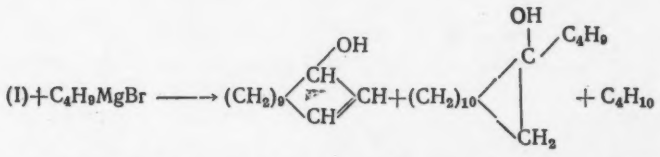
In the course of an investigation of the properties of derivatives of cyclododecane, we have studied the action of n-butyllithium and n-butylmagnesium bromide on trans-epoxycyclododecane (I) and trans-epoxy-cis, trans-cyclododeca-5,9-diene (II). An interesting rearrangement of the α-epoxide under the influence of organolithium and -magnesium compounds was discovered. It was found that when (I) reacts with butyllithium in ethereal solution, butane is evolved and, instead of the expected reaction product 2-butylcyclododecanol, 1-hydroxycyclododec-2-ene is formed



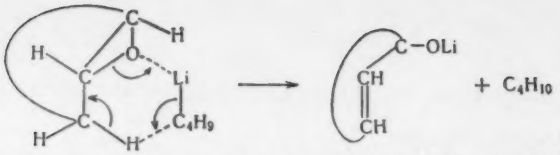
The 1-hydroxycyclododec-2-ene produced consists of a mixture of cis and trans isomers, from which the crystalline 1-hydroxy-cis-cyclododec-2-ene separates on standing. On hydrogenating 1-hydroxycyclododec-2-ene, cyclododecanol is obtained quantitatively. The reaction of (II) with butyllithium takes place in a similar manner, giving butane and 1-hydroxycyclododeca-2,5,9-triene



The 1-hydroxycyclododeca-2,5,9-triene obtained in this reaction is a mixture of isomers from which an isomer with 74-75° crystallizes out. On hydrogenating 1-hydroxycyclododeca-2,5,9-triene, three moles of hydrogen are absorbed and cyclododecanol is formed. Recently, Kirchhof [1] reported a similar isomerization in the reactions of (I) and (II) with diisobutylaluminium hydride. The reaction of butylmagnesium bromide with (I) also leads to the liberation of butane; however, in addition to 1-hydroxycyclododec-2-ene, 1-butyl-1-hydroxycyclododecane is formed; i.e., in this case the reaction proceeds according to the scheme



The structure of 1-butyl-1-hydroxycyclododecane is shown by its synthesis from cyclododecanone and butylmagnesium bromide. Isomerization of (I) under the action of butyllithium apparently takes place by a mechanism analogous to the splitting out of ethers under the action of organolithium compounds or through a six-membered intermediate complex



Isomerization under the action of butylmagnesium bromide probably takes place by the latter mechanism also.

EXPERIMENTAL PART

Action of butyllithium on trans-epoxycyclododecane. To an ethereal solution of butyllithium (from 3.2 g of lithium and 30 g of butyl bromide), 30 g of trans-epoxycyclododecane [2] was added during 5 min. Slow ebullition of the ether took place from the heat of reaction, butane being evolved. After heating for 5 hours, ~ 10 g of butane had been evolved. The cooled reaction mixture was decomposed with water. The ethereal layer was dried over potash. On vacuum distillation, 24.3 g of 1-hydroxycyclododec-2-ene with b.p. 110-112° (3 mm); n^{20}_D 1.4925 was obtained. Found: C 79.23; 79.29; H 12.29; 12.22% $C_{12}H_{22}O$. Calculated: C 79.12; H 12.11%

When the 1-hydroxycyclododec-2-ene obtained was allowed to stand, crystals of 1-hydroxy-cis-cyclododec-2-ene with m.p. 69-70° (from petroleum ether) separated out. Literature data [1]: m.p. 69.6-69.0°. Found: C 79.17; 79.29; H 12.14; 12.23% $C_{12}H_{22}O$. Calculated: C79.12; H 12.11%

On hydrogenating the mixture of isomers of 1-hydroxycyclododec-2-ene or 1-hydroxy-cis-cyclododec-2-ene over $Pd/BaSO_4$ in acetic acid solution, cyclododecanol with m.p. 79-80, giving no depression of the melting point in admixture with a known sample, was obtained.

Action of butyllithium on trans-epoxy-cis, trans-cyclododeca-5,9-diene. To an ethereal solution of butyllithium (from 3.3 g of lithium and 30 g of butyl bromide), 30 g of trans-epoxy-cis, trans-cyclododeca-5,9-diene [2] was added over 50 min. The reaction took place with the evolution of heat. About 10.5 g of butane was liberated. After working up as in the previous experiment, on vacuum distillation 20.1 g of 1-hydroxycyclododeca-2,5,9-triene was obtained with b.p. 114-117° (4 mm); n^{20}_D 1.5243. Found: C 80.92; 81.04; H 10.26; 12.23% $C_{12}H_{18}O$. Calculated: C 80.90; H 10.11%

The residue boiled above 200° at 4 mm. When the 1-hydroxycyclododeca-2,5,9-triene was allowed to stand, it largely crystallized. The crystalline isomer, apparently with two cis and one trans bonds, had m.p. 74-75° (from petroleum ether). Literature data [1]: m.p. 74-74.6°. Found: C 80.94; 80.71; H 10.21; 9.99% $C_{12}H_{18}O$. Calculated: C 80.90; H 10.11%

On hydrogenating the mixture of isomers or the crystalline isomer over $Pd/BaSO_4$ in acetic acid solution, cyclododecanol was obtained, m.p. 79-80°.

Action of butylmagnesium bromide on trans-epoxycyclododecane. To an ethereal solution of butylmagnesium bromide (from 6.5 g of magnesium and 35 g of butyl bromide), 30 g of trans-epoxycyclododecane was added. No rise in temperature was observed. The ether was distilled off on the water bath. After the removal of a large part of the ether, pronounced foaming took place, and the ether boiled strongly. The ether was removed completely on the boiling water bath and the residue was then heated for a further 1 hour. The evolution of 4.8 g of butane took place. The residue was dissolved in ether and decomposed with dilute hydrochloric acid. The ethereal solution was dried over potash. On distillation, 10.1 g of 1-hydroxycyclododec-2-ene was obtained, with b.p. 112-114° (3 mm); n^{20}_D 1.4927, and 16.3 g of 1-hydroxy-1-butylcyclododecane with b.p. 145-148° (3 mm); m.p. 72° (from petroleum ether). Found: C 79.91; 80.06; H 13.39; 13.53% $C_{16}H_{32}O$. Calculated: C 80.01; H 13.33%

The 1-hydroxy-1-butylcyclododecane gave no depression of the melting point in admixture with 1-hydroxy-1-butylcyclododecane obtained by the usual method from cyclododecanone and butylmagnesium bromide. On standing, the 1-hydroxycyclododec-2-ene obtained gave the crystalline isomer with m.p. 69-70° identical with that from the experiment with butyllithium.

SUMMARY

Using epoxycyclododecane and epoxycyclododeca-5,9-diene as examples, it has been found that α-epoxides undergo isomerization to unsaturated alcohols under the action of organolithium and -magnesium compounds.

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A SIMPLE METHOD FOR THE PREPARATION OF SODIUM AND POTASSIUM ALUMINIUM HYDRIDES

L. I. Zakharkin and V. V. Gavrilenko

The Institute of Heteroorganic Compounds of the Academy of Sciences of the USSR
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Sodium aluminium hydride $NaAlH_4$ is analogous in its reducing properties to lithium aluminium hydride, widely used at the present time [1]. The use of sodium aluminium hydride, which should be considerably cheaper than lithium aluminium hydride, is hindered by the absence of convenient and simple methods for preparing it. The two-stage process for preparing sodium aluminium hydride according to the scheme

$$3NaAlH_4 + AlCl_3 \longrightarrow 4AlH_3 + 3NaCl$$

$$4AlH_3 + 4NaH \longrightarrow 4NaAlH_4$$

described by Finholt, Schlesinger, and co-workers [2] is complicated and requires the use of very pure reactants, and necessitates working with unstable aluminium hydride. Another method of preparing sodium aluminium hydride, developed by Vit, Prochazka, and Petru [3] consists in the action of a benzene solution of aluminium bromide on sodium hydride in tetrahydrofurane, the use of freshly-prepared sodium hydride being essential. According to data of Finholt, Schlesinger, et al. [2], aluminium bromide reacts very slowly with sodium hydride and the yield of sodium aluminium hydride does not exceed 60%. To obtain large amounts of sodium aluminium hydride, the use of aluminium bromide is disadvantageous. As Finholt, Schlesinger, et al. [2] indicate, the direct interaction of sodium hydride with aluminium chloride in solution in tetrahydrofurane and other solvents (diethyl ether, the dimethyl ether of ethylene glycol, the dimethyl ether of triethyleneglycol, etc.) takes place very slowly, is accompanied by the decomposition of the solvent and cannot be used to prepare sodium aluminium hydride.

In the present work it was found that sodium aluminium hydride may be readily obtained with high yields from aluminium chloride and sodium hydride in one stage in the presence of catalytic amounts of trialkylaluminiums, dialkylaluminium hydrides, or their complexes with sodium hydride. According to this method, 2-4% of a trialkylaluminium, for example, triethylaluminium or triisobutylaluminium, or the corresponding dialkylaluminium hydride, is added to a suspension of sodium hydride in benzene. The mixture is heated to 60-80° and a concentrated solution of aluminium chloride in diethyl ether is added to it with stirring. The temperature is maintained in the range 65-75° by the heat of the reaction. The reaction takes place rapidly. After the completion of the reaction, the reaction mixture is centrifuged or filtered. The filtrate contains all the catalyst in the form of a complex with sodium hydride and it may be used again for the preparation of a further batch of sodium aluminium hydride. The sodium aluminium hydride is extracted from the solid residue with tetrahydrofurane or another suitable solvent. The yield of sodium aluminium hydride amounts to more than 90% of theory.

The role of the organoaluminium compounds in this reaction consists in the conversion of the sodium hydride into the dissolved state in the form of the complexes $NaH \cdot AlR_3$ or $NaH \cdot AlR_2H$, which also effect the reduction of the aluminium chloride, for example according to the scheme

$$(C_2H_5)_3Al + NaH \longrightarrow NaH(C_2H_5)_3Al$$

$$3NaH(C_2H_5)_3Al + AlCl_3 \longrightarrow AlH_3 + 3(C_2H_5)_3Al + 3NaCl$$

$$AlH_3 + NaH \longrightarrow NaAlH_4$$

We have also used this method for synthesis of potassium aluminium hydride from aluminium chloride and potassium hydride. Diisobutylaluminium hydride was used as the catalyst. Potassium aluminium hydride consists of a infusible white crystalline substance decomposing at temperatures above 260°.

EXPERIMENTAL PART

Preparation of sodium aluminium hydride. A 5000-ml four-necked flask with a mixer, reflux condenser, dropping funnel, and thermometer, was charged with 330 g of sodium hydride and 800 ml of dry benzene. After the flask had been filled with nitrogen, 15 g of triethylaluminium was added and the contents of the flask were warmed to 70° with stirring. At this temperature, an ethereal solution of aluminium chloride obtained from 400 g of $AlCl_3$ and 500 ml of absolute ether was added uniformly from the dropping funnel. It is necessary that the aluminium chloride solution should not strike the wall of the flask. It is desirable to add the aluminium chloride solution close to the center of the flask, with good stirring.

The last quarter of the minimum fluoride solution must be added at a more moderate rate and with more vigorous stirring in order not to create a high concentration of aluminium chloride, the solution is stirred for a further 0.5-1 hour. The time for the whole operation is 3-4 hours. The suspension formed is centrifuged. The benzene-ether solution removes the whole of the catalyst in the form of a complex with sodium hydride. The solid residue is treated with tetrahydrofurane at the rate of approximately 100 ml of solvent per 2 g of sodium aluminium hydride and centrifuged. The clarified tetrahydrofurane solution, after evaporation, deposited coarse crystals of sodium aluminium hydride, which were filtered off and washed with ether. A yield of 147 g of $NaAlH_4$ (91%) was obtained; decomposition temperature in the range 190-250°. Found: Al 49.85; 49.86% $NaAlH_4$. Calculated: Al 49.96%

Preparation of potassium aluminium hydride. In a similar way potassium aluminium hydride was obtained from 30 g of potassium hydride in 120 ml of benzene and 20.5 g of aluminium chloride dissolved in 25 ml of ether, using 2 g of diisobutylaluminium hydride as the catalyst; it was extracted from the solid residue after removal of the benzene-ether solution with the dimethyl ether of diethyleneglycol. After evaporating the solvent in vacuum, 9 g of potassium aluminium hydride was obtained in the form of a white crystalline powder decomposing on heating within the range 260-270° without melting. Found: Al 38.08; 38.10% $KAlH_4$. Calculated: Al 38.48%

SUMMARY

Sodium and potassium aluminium hydrides are readily obtained from aluminium chloride and sodium and potassium hydrides, respectively, using organoaluminium compounds as catalysts for the reaction.

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PREPARATION OF 1-CYCLOPROPYL-2-(4'-HYDROXY-1'-OXOBUTYL)-CYCLOPROPANE

A. P. Meshcheryakov and V. G. Glukhovtsev

The N. D. Zelinskii Institute of Organic Chemistry of the Academy of Sciences of the USSR
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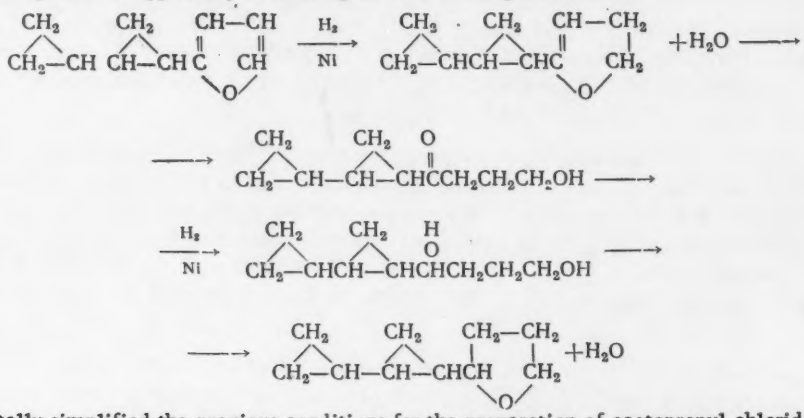
We have shown [1] that in the hydrogenation of 1-cyclopropyl-2-α-tetrahydrofurylcyclopropane is formed with a yield of 39%. In the present work it was found that at normal pressure and room temperature the process takes place extremely slowly and the sole product of the reaction is 1-cyclopropyl-2-(4'-hydroxy-1'-oxobutyl)-cyclopropane, formed through the addition of molecules of hydrogen and water. In addition, it was found that, when water was added, hydrogenation under the conditions described in [1] go considerably faster and more completely. Under these conditions, in addition of 1-cyclopropyl-2-α-tetrahydrofurylcyclopropane, 1-cyclopropyl-2-(4'-hydroxy-1'-oxobutyl)-cyclopropyl-2-α-furylcyclopropane proceeds, apparently, according to the following scheme:



We have fundamentally simplified the previous conditions for the preparation of acetopropyl chloride and methyl cyclopropyl ketone—the starting materials for the synthesis of 1-cyclopropyl-2-α-furylcyclopropane. It has been established that the conditions found for closing the cyclopropyl ring by the action of dry caustic potash on a γ-chloride are general for the preparation of a dicyclopropyl ketone.

As a result of the reduction by Kizhner's method of the keto group in 1-cyclopropyl-2-(4'-hydroxy-1'-oxobutyl)-cyclopropane, an alcohol was obtained containing two cyclopropyl rings in the molecule. Since the replacement of the hydroxyl group by chlorine in cyclopropane compounds is generally accompanied by isomerization of the cyclopropyl ring [2], conditions were worked out, using methyl cyclopropyl carbinol as an example, which avoid the opening of the cyclopropyl ring. Under these conditions, a primary chloride with two cyclopropyl rings in the molecule was successfully obtained. The reaction of this chloride with sodium in ether led to the production of 1-cyclopropyl-2-butylcyclopropane.

EXPERIMENTAL PART

Acetopropyl chloride. Hydrochloric acid (440 ml) was saturated with hydrogen chloride (from 270 ml of HCl and 300 ml of H_2SO_4) during 1 hour, with stirring and cooling to -10°. Then 213 g of acetopropyl alcohol with b.p. 87-88° (6 mm) and n_D^{20} 1.4415, cooled to -5°, was added over 45 minutes to the cooled flask. After stirring the reaction mixture for an hour, cooling was discontinued. After 2 hours, 400 ml of water was added to the flask and the acetopropyl chloride was obtained, with b.p. 69° (19 mm); n_D^{17} 1.4390; yield 75.5%.

Methyl cyclopropyl ketone was obtained from acetopropyl chloride by the method described earlier [3], but without the use of ether for its extraction. Salting-out instead of extraction scarcely diminished the yield of methyl cyclopropyl ketone.

Dicyclopropyl ketone. 1,7-Dichloroheptan-4-one [4] with b.p. 104-110° (4 mm) (85 g) was added with shaking to 160 g of granulated KOH. Then the mixture was heated for 2 hours on the boiling water bath, after which 250 ml of water was added to the flask. After cooling, the upper layer was separated off and dried with KOH, and the lower layer was extracted three times with 40-ml portions of ether. After distilling off the ether, the residue, together with the upper layer, was distilled in vacuum. A yield of 43.5 g of dicyclopropyl ketone was obtained, with b.p. 67° (26 mm); n_D^{20} 1.4682; d_4^{20} 0.9646; found: MR 31.75; calculated: MR 31.61.

Raman spectrum ($\Delta\nu$ cm^{-1}): 202 (1); 246(1); 365(2 broad); 474 (2); 534 (1); 633 (very broad); 728 (2 broad); 753 (5); 814 (10); 842 (1 broad); 923 (10); 1037 (5); 1060 (1); 1096 (2 broad); 1105 (3 broad); 1142 (2 sharp); 1178 (3); 1200 (10); 1247 (0); 1295 (0); 1348 (8); 1382 (10); 1417 (2); 1450 (7); 1682 (6); 2872 (0); 2913 (1); 2950 (2); 3010 (10); 3075 (6 broad).

Methylcyclopropylcarbinol [5] was obtained by hydrogenating methyl cyclopropyl ketone over Raney nickel at 40° and ~120 atmospheres of H_2 with a yield of 85%; b.p. 122-122.5°, n_D^{20} 1.4318.

Methyl cyclopropyl carbinyl chloride. A mixture of 23 g of PCl_3, 1 g of dimethylaniline, and 50 ml of absolute ether was added to a mixture of 43 g of methyl cyclopropyl carbinol, 20 g of dimethylaniline, and 100 ml of absolute ether during 1 hour, with stirring and cooling to -10°. Then the ethereal solution was poured off the precipitate and the residue was washed with ether. After distilling off the ether, the residue was distilled in vacuum. A yield of 26.1 g of methyl cyclopropyl carbinyl chloride was obtained, with b.p. 50° (136 mm); 101° (760 mm); n_D^{20} 1.4320; d_4^{20} 0.9419; yield 50%. Found: C 57.42; H 8.67; Cl 33.9%. MR 28.68.

Raman Spectrum ($\Delta\nu$ cm^{-1}): 282 (2 broad); 312 (2); 336 (1); 393 (10); 498 (0); 592 (very broad); 643, 659 (5 broad, 10 broad); 710 (0); 768 (3 broad); 824 (3 broad); 908 (7 broad); 1007, 1037 (2 broad, 3 broad); 1093 (1 broad); 1187, 1198 (4, 10); 1218 (2); 1238 (2 broad); 1298 (2); 1394 (4); 1432, 1447 (3 broad, 3 broad); 1465 (3 broad); 2873 (3 broad); 2930 (8 broad); 3010 (10); 3078 (4 broad).

1-Cyclopropyl-2-α-tetrahydrofurylcyclopropane. A mixture of 144 g of 1-cyclopropyl-2-furylcyclopropane, 200 ml of C_2H_5OH, 30 ml of H_2O, and 10 g of Raney nickel was heated to 70° with hydrogen (120 atm.) in a liter autoclave with stirring until 52 atmosphers of hydrogen had been adsorbed. After the usual working up [1], 103 g (69%) of 1-cyclopropyl-2-α-tetrahydrofurylcyclopropane was obtained, together with 20 g of 1-cyclopropyl-2-(4'-hydroxy-1'-oxobutyl)-cyclopropane, with b.p. 130° (3 mm); n_D^{20} 1.4845; d_4^{20} 1.0212; yield 12.3% Found: C 71.75; 71.65; H 9.80; 9.67% MR 47.16. $C_{10}H_{16}O_2$. Calculated: C 71.39; H 9.58% MR 47.00. Number of atoms of active hydrogen found: 1.2; 1.1; 1.1.

Raman spectrum ($\Delta\nu$ cm^{-1}): 263 (1 broad); 400 (3 broad); 735 (5 broad); 792 (4 broad); 812 (4 broad); 842 (3 broad); 885 (3 broad); 932 (5 broad); 966 (4 broad); 1040 (4 broad); 1102 (1 broad); 1036 (3 broad); 1195 (6); 1240 (6); 1295 (1 broad); 1410 (3 broad); 1435 (4 broad); 1457 (3 broad); 1685 (2 broad); 3046 (3 broad).

1-Cyclopropyl-2-(4'-hydroxybutyl)-cyclopropane. A mixture of 25 g of 1-cyclopropyl-2-(4'-hydroxy-1'-oxobutyl)-cyclopropane, 15 g of hydrazine hydrate, and 20 ml of C_2H_5OH was boiled for 10 hours under reflux. After distilling off the alcohol and the hydrazine hydrate, the residue was distilled in vacuum. A yield of 26.8 g of the alkylidenehydrazine was obtained, with b.p. 158-165° (5 mm); n_D^{20} 1.5210; d_4^{20} 1.045; yield 99% The alkylidenehydrazine (23 g) was slowly distilled over 3 g of KOH. A yield of 15 g of 1-cyclopropyl-2-(4'-hydroxybutyl)-cyclopropane was obtained, with b.p. 102° (5 mm); n_D^{20} 1.4650; d_4^{20} 0.9120. Found: C 77.32; 77.15; H 11.52; 11.59% MR 46.73. $C_{10}H_{18}O$. Calculated: C 77.86; H 11.76% MR 47.03.

Raman spectrum ($\Delta\nu$ cm^{-1}): 198 (0); 365 (0); 455 (0); 712 (2 broad); 730, 743 (2 broad, 2 broad); 775 (3 broad); 810 (1 broad); 815 (3 broad); 832 (1 broad); 865 (3), 895, 910 (2 broad, 2 broad); 952 (3); 975 (1 broad); 1020 (2 broad); 1073 (2 broad); 1127 (2 broad); 1170 (3); 1188 (4); 1225 (6); 1296 (3); 1322 (1); 1372 (2); 1405 (5); 1435 (5); 1460 (6); 2855 (5 broad); 2903 (6); 2938 (3); 3002 (10); 3070 (5).

1-Cyclopropyl-2-(4'-chlorobutyl)-cyclopropane. A mixture of 5.5 g of PCl_3, 1 g of pyridine, and 50 ml of ether was added to a mixture of 18 g of 1-cyclopropyl-2-(4'hydroxybutyl)-cyclopropane, 5 g of pyridine, and 50 ml of ether with stirring and cooling to -10°. After 2 hours' stirring, the liquid was poured off from the precipitate and the residue was washed with ether. After the ether had been distilled off, the residue was distilled in vacuum. A yield of 4 g (20%) of 1-cyclopropyl-2-(4'-chlorobutyl)cyclopropane was obtained, with b.p. 85° (6 mm); n_D^{20} 1.4649; d_4^{20} 0.953. Found: C 69.64; 69.68; H 9.93; 10.03; Cl 20.54; 20.44% MR 50.08. $C_{10}H_{17}Cl$. Calculated: C 69.54; H 9.91; Cl 20.53% MR 50.42.

1-Cyclopropyl-2-butylcyclopropane. A mixture of 2.5 g of 1-cyclopropyl-2-(4'-chlorobutyl)-cyclopropane and 3 g of sodium in 15 ml of ether was boiled for 10 hours under reflux. After distilling off the ether, the residue was distilled in vacuum. A yield of 1 g of 1-cyclopropyl-2-butylcyclopropane was obtained, with b.p. 55° (10 mm); n_D^{20} 1.4376; d_4^{20} 0.8017; yield 50% Found: C 87.23; 86.95; H 12.90; 13.10% MR 45.22. $C_{10}H_{18}$. Calculated: C 86.87; H 13.12% MR 45.58.

SUMMARY

1. Over Raney nickel in the presence of water, the hydrogenation of the furyl ring in 1-cyclopropyl-2-α-furyl-cyclopropane is accompanied by its hydration without rupture of the cyclopropyl rings.

2. 1-Cyclopropyl-2-(4'-hydroxy-1'-oxobutyl)-cyclopropane, 1-cyclopropyl-2-(4'hydroxybutyl)-cyclopropane, 1-cyclopropyl-2-(4'-chlorobutyl)-cyclopropane, and 1-cyclopropyl-2-butylcyclopropane have been obtained for the first time.

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SYNTHESIS OF 3,3,4-TRIMETHYLPENT-1-YNE AND 2,3,3,8,8,9-HEXAMETHYLDECA-4,6-DIYNE

A. P. Meshcheryakov and L. V. Petrova

The N. D. Zelinskii Institute of Organic Chemistry of the Academy of Sciences of the USSR

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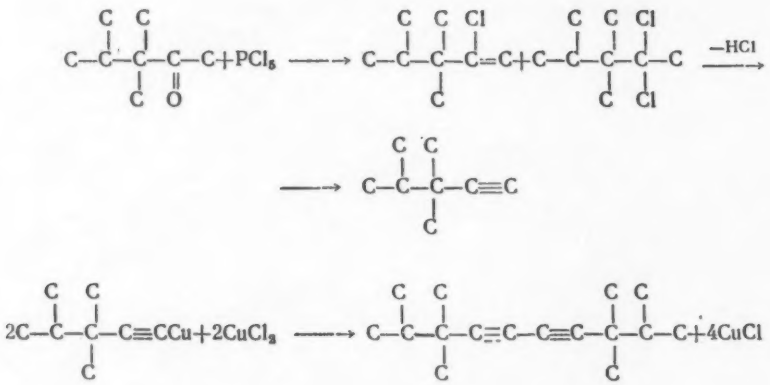
Diacetylenic hydrocarbons (derivatives of diacetylene) have been obtained by the oxidation of the copper [1, 2,3] and magnesium bromide derivatives of monosubstituted acetylenes [4] with various oxidizing agents. Favorskii [5] obtained di-t-butylacetylene by oxidizing the copper derivative of t-butylacetylene with potassium ferricyanide. Zal'kind [6], in a similar manner to Glaser [1] and Griner [3], obtained diphenylacetylene by the method of oxidative-reductive dimerization of phenylacetylene in ammoniacal solution with cuprous chloride; he used this method for the production of diacetylenic glycols from acetylenic alcohols. As is well known, mono- and dichlorides of ketones are used for the preparation of acetylenic hydrocarbons. From 3,3,4-trimethylpentane-2-one, by reaction with PCl_5, we have obtained the mono- and dichlorides of the ketone: 2-chloro-3,3,4-trimethylpent-1-ene and 2,2-dichloro-3,3,4-trimethylpentane. By splitting out one molecule of hydrogen chloride in the first case and two in the second case, we obtained 3,3,4-trimethylpent-1-yne (I). By the oxidative dimerization of 3,3,4-trimethylpent-1-yne, the dimer 2,3,3,8,8,9-hexamethyldeca-4,6-diyne (II) was obtained.



EXPERIMENTAL PART

3,3,4-Trimethylpent-1-yne (I). The initial 3,3,4-trimethylpentan-2-one (b.p. 150-152°) was obtained by the hydrogenation of 3,3,4-trimethylpent-4-en-2-one over a catalyst of 5% Pt on carbon. The unsaturated ketone was synthesized from tetramethylethylene and acetic anhydride in the presence of zinc chloride according to Kondakov [7]. The 3,3,4-trimethylpentan-2-one was treated with PCl_5, and after two distillations the following were isolated:

a) The monochloride – 3,3,4-trimethyl-2-chloropent-1-ene, yield 50%; b.p. 150-153°; d_4^{20} 0.9156; n_D^{20} 1.4530; found MR 43.20; calculated MR 43.54. Found: Cl 25.77%; $C_8H_{15}Cl$. Calculated: Cl 24.00%

b) The dichloride – 3,3,4-trimethyl-2-2-dichloropentane (yield 30%); b.p. 76-78° (15 mm); d_4^{20} 1.0509; n_D^{20} 1.4715. Found MR 48.45. Calculated MR 48.87. Found: Cl 38.44%; $C_8H_{16}Cl_2$. Calculated: Cl 38.45%

To obtain the acetylenic hydrocarbon, the chlorides were heated with alcoholic alkali (KOH) at 180-220° in a silicone bath for 12 hours. Distillation in a column of 24 theoretical plates yielded 3,3,4-trimethylpent-1-yne (I) with a yield of 50% on the chloride taken.

The hydrocarbon gave the test for acetylenic hydrogen with a solution of cuprous chloride and silver nitrate: b.p. 97-98°; d_4^{20} 0.7446; n_D^{20} 1.4120; found MR 36.73; calculated MR 37.08. Found: C 87.12; H 12.80% C_8H_{14}. Calculated: C 87.27; H 12.73%

Raman Spectrum: 152 (10 broad); 182 (10); 330 (1); 368 (0); 390 (1); 423 (1); 433 (1); 449 (1); 598 (1); 632 (2 broad); 658 (10); 680 (5); 828 (2 broad); 877 (0 broad); 915 (0); 946 (5 broad); 1061 (1 broad); 1107 (2 broad); 1178 (4 broad); 1218 (2 broad); 1235 (2 broad); 1330 (2 broad); 1386 (1 broad); 1450 (5 broad); 1463 (8 broad); 1632 (0); 2052 (2); 2112 (10); 2888 (5 broad); 2920 (3 broad); 2942 (3 broad); 2983 (10 broad).

2,3,4,8,8,9-Hexamethyldeca-4,6-diyne (II). The hydrocarbon was obtained by the oxidative dimerization of 3,3,-4-trimethylpent-1-yne by the method described by Zal'kind and Fundyler [6] with a yield of 50% on the monomer taken. To a boiling mixture of 90 g of cuprous chloride, 140 g of ammonium chloride, 375 ml of water, and 2 g of hydrochloric acid (sp.gr. 1.19) was added 19 g of 3,3,4-trimethylpent-1-yne during 30 min., and then the whole was heating to boiling for 8 hours. The hydrocarbon was extracted from the solid complex with ether, the latter was distilled off, and the solid hydrocarbon was recrystallized from methyl alcohol; m.p. 134-134.5°; yield 50.5% on the 3,3,4-trimethylpent-1-yne taken. Found: C 87.45; H 12.09% $C_{16}H_{26}$. Calculated: C 88.10; H 11.90%

SUMMARY

1. The mono- and dichlorides of 3,3,4-trimethylpentan-2-one and the acetylenic hydrocarbon 3,3,4-trimethylpent-1-yne have been obtained for the first time.

2. The diacetylenic hydrocarbon 2,3,3,8,8,9-hexamethyldeca-4,6-diyne has been obtained by the oxidative-reductive dimerization of 3,3,4-trimethylpent-1-yne.

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CONJUGATION ENERGY OF SOME BORON-CONTAINING SYSTEMS

D. A. Bochvar, I. V. Stankevich, and A. L. Chistyakov

The Institute of Heteroorganic Compounds of the Academy of Science
of the USSR
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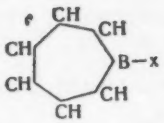
The results of an earlier calculation of the conjugation enery for the molecule of borepin, which indicated the high probability of a considerable conjugation energy in the molecule of borepin, together with the recent synthesis [2] of benzo derivatives of borepin, on the one hand,

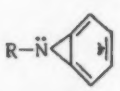


and, on the other hand, the results of a calculation of the conjugation energy for the experimentally obtained phenyl derivatives of the propenyl cation provoke interest in a heterocyclic conjugated system containing boron as the heteroatom (possibly together with a heteroatom capable of playing an electron donor function) and, at the same time, possessing strained valency angles.

In view of the question put in this way, we have carried out calculations by the MO LCAO method, in Hückel's π-electron approximation, of a number of concrete conjugated systems of this type or systems which were of interest for comparison. The following symbolism was used: $\alpha = \alpha_C$ – the Coulomb integral for an atom of C; α_x – the Coulomb integral for an atom x; α_y the Coulomb integral for an atom y; β_{CC} – the resonance integral for a C–C bond; β_{Cx} – the resonance integral for a C–x bond; β_{Cy} – the resonance integral for a C–y bond; the parameters g_1, g_2, h_1, h_2 and h_3 were determined by the corresponding equations: $\alpha_x = \alpha + g_1\beta$; $\beta_y = \alpha + g_2\beta$; $\beta_{Cx} = h_1\beta$; $\beta_{Cy} = h_2\beta$; and $\beta_{xy} = h_3\beta$.

The main results are given below.

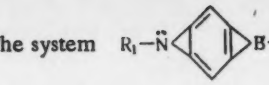
I. The system (the R–N bond is a σ-bond and is not taken into consideration in the calculation)



for $h_1 = 1$, $g_1 = 1$ (x = N) has 4 bonding orbitals and 8 π-electrons; the conjugation energy in comparison with the phenyl ring and the pair of electrons of the nitrogen ("pyrrole" nitrogen) is 0.39β. For $h_1 = 0.9$; $g_1 = 1.0$ (see [3]), the conjugation energy is 0.32β [the value of β is generally estimated as 0.7-0.8 eV].

II. The system R_1–N⟨⟩C^+–R_2 – the cation is more conveniently represented by the formula

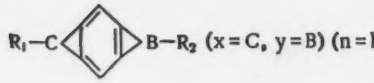
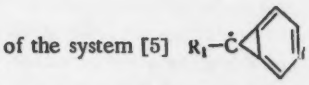
R_1–N⟨(+)⟩C–R_2 – where x = N; y = C; $h_1 = 1$; $h_2 = 1$; $g_1 = 1$; $g_2 = 0$, contains 4 bonding molecular orbitals and 8 π-electrons and has an energy $\varepsilon = 2.0\beta$ (above the conjugation energy for system I). From the point of view of the properties of a π-electron system, the cation is stable.

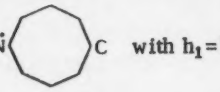
III. The system  with $h_1 = 1$; $h_2 = 1$; $g_1 = 1$; $g_2 = -7$ [at a value of -4, the energy rises considerably] contains 4 bonding orbitals and 8 π-electrons and, compared with system I, has a gain in energy of 0.54β.

IV. The system [the dimer of system III]: ($h_1 = h_2 = h_3 = 1$; $g_1 = 1$; $g_2 = -7$] has 8 bonding orbitals and 16 π-electrons. The conjugation energy in excess of double the conjugation energy of system III is 0.85β. Thus, from the point of view of the properties of the π-electron system, IV is considerably more stable than III. A further increase in the number of rings in the chain on polymerization must continue to increase the conjugation energy. This is due to the increase in the number of bonds of the borazole type and their conjugation with the π-electrons of the ring systems. The calculation, of course, does not take into account the fact that on dimerization the $N-R_1$ and $B-R_2$ bonds are ruptured; a $B-N$ σ bond and some σ bonds at R_1 and R_2 appear. However, it is undoubtedly possible to choose R_1 and R_2 for which the energies of rupture and of formation of the σ bonds mentioned mutually compensate one another; the calculation, of course, does not take the strain of the valency angles into account.

For the choice of $h_3 = 3$ (see [4]) the conjugation energy ε proves to be much greater, namely, in this case, $\varepsilon = 2.52\beta$. However, it is more probable that these values of h_3 and ε are too high.

V. The system (free radical)

 ($x = C$, $y = B$) ($n = h_2 = 1$; $g_1 = 0$; $g_2 = -7$) has 3 bonding molecular orbitals and 7 π-electrons. The conjugation energy above the energy of the system [5]  is 0.78β and that above the sum of the conjugation energies of the phenyl ring and α_C is 2.02β. The high conjugation energy is connected with the pronounced delocalization of the free electron and the effective charges on the atoms ($+\delta$ on C and $-\delta$ on B), the positive effective charge being possibly also delocalized and distributed over the C atoms.

VI. The system (cation) ($x = C$, $y = N$)  with $h_1 = h_2 = 1$; $g_2 = 0$; $g_1 = 1$ contains 4 bonding molecular orbitals and 8 π-electrons. The conjugation energy above the sum of the conjugation energy of hexatriene and $2\alpha_N$ is 2.19β, i.e., it is extremely considerable and the cation may be stable.

SUMMARY

The conjugation energies of some boron-containing heterocyclic compounds have been calculated. In a number of cases, in spite of the unusual valency angles, within the framework of the MO LCAO method in the π-electron approximation, these systems prove to be stable.

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3. A. Pullman, and B. Pullman, Rev. Mod. Phys. 32, 2, 482 (1960).
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LETTERS TO THE EDITORS

THE SYNTHESIS OF ORGANOBERYLLIUM COMPOUNDS

L. I. Zakharkin, O. Yu. Okhlobystin, and B. N. Strunik

Institute of Heteroorganic Chemistry of the Academy of Sciences of the USSR
Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk,
No. 12, pp. 2254, December, 1961
Original article submitted October 26, 1961

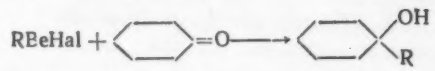
According to Gilman's results, powdered beryllium, in contrast to magnesium, reacts with alkyl halides with difficulty and only on long heating in the presence of ether and special catalysts—mercuric chloride and beryllium chloride [1]. Under these conditions, the formation of organoberyllium compounds was shown by Gilman only qualitatively by the color test with Michler's ketone. This method received no further development.

In studying the uncatalyzed reaction of metals of group II with alkyl halides, we found that powdered beryllium reacts with alkyl halides even in the complete absence of ether and any catalysts whatever, giving, after a sufficiently long time, alkyl beryllium halides in satisfactory yields:

$$Be + RHal \xrightarrow[12-60\ hr]{130^\circ} RBeHal$$

$R=C_2H_5$, Hal=I; $R=C_4H_9$, Hal=Br, I, $R=C_5H_{11}$, C_8H_{17}, Hal=I.

Like the alkyl magnesium halides, the alkyl beryllium halides are insoluble in alkyl halides and separate out during the reaction in the form of a precipitate. From the analytical data, the yield of butylberyllium iodide amounted to 65-70% of theory (130°, 12 hours, without solvent). When the alkyl beryllium halides reacted with cyclohexanone, the corresponding 1-alkylcyclohexanols were formed in good yield



$R=C_2H_5$, b.p. 61° (10 mm), n_D^{25} 1.4623; d_4^{25} 0.9226; $R=C_4H_9$, b.p. 90-91° (10 mm); n_D^{25} 1.4635; d_4^{25} 0.9141; $R=C_5H_{11}$, b.p. 97° (5 mm); n_D^{20} 1.4667; d_4^{20} 0.9162; $R=C_8H_{17}$, b.p. 130-131° (10 mm); n_D^{25} 1.4610; d_4^{25} 0.8633.

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ORGANOMAGNESIUM SYNTHESIS OF HETEROORGANIC COMPOUNDS IN A NON-ETHEREAL MEDIUM

L. I. Zakharkin, O. Yu. Okhlobystin, and B. N. Strunin

Institute of Heteroorganic Chemistry of the Academy of Sciences of the USSR
Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk,
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Contradictory information exists on the possibility of the non-catalyzed reaction of magnesium with alkyl halides. In a number of foreign investigations [1], the fact that such a synthesis is possible in principle has been demonstrated. Later, Shorygin and co-workers reported the specific characteristic of halogenobenzenes of reacting with magnesium under severe conditions in the absence of a catalyst for the Grignard reaction and asserted that a similar reaction with alkyl halides was impossible [2]. In 1958, Zakharkin and Okhlobystin prepared trialkylborons from alkyl metaborates by the direct organomagnesium synthesis in toluene in the complete absence of catalysts for the Grignard reaction [3]. Recently, Bryce-Smith [4] has reported that magnesium reacts in a non-ethereal medium with alkyl iodides in isopropylbenzene.

In studying the mechanism of the non-catalyzed organomagnesium synthesis, we found that magnesium reacts readily and exothermically with alkyl halides both in the total absence of a solvent and in various aliphatic hydrocarbons, and specific solvents of the type of isopropylbenzene are in no way necessary. We have used the non-ethereal organomagnesium synthesis for the preparation of diverse heteroorganic compounds, exemplified by the one- and two-stage synthesis of (aryl) derivatives of a number of elements:

$$\ni X_n + n\,RMgX \longrightarrow \ni R_n + nMgX_2$$

$$\ni X_n + n\,Mg + nRX \longrightarrow \ni R_n + nMgX_2$$

R = C_2H_5; p-C_4H_9; *i*-C_5H_{11}; p-C_6H_{13}; p-C_8H_{17}; C_6H_5; ∋ = Hg, B, Al, Sn, Ge, Si, Sb, P, As; Hal = Cl, Br, I.

The yields of heteroorganic compounds amounted to 70-90%.

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3. L. I. Zakharkin, and O. Yu. Okhlobystin, Izv. AN SSSR, 1135(1959).
4. D. Bryce-Smith and G. Cox, J. Chem. Soc. 1175(1961).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

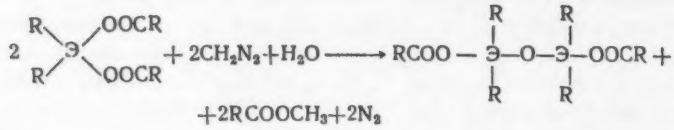
STEPWISE FORMATION OF A HETEROELEMENT – OXYGEN CHAIN IN THE PRESENCE OF DIAZOALKANES

K. A. Kocheshkov, E. M. Panov, and N. N. Zemlyanskii

The L. Ya. Karpov Physicochemical Institute

Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 12, p. 2255, December, 1961
Original article submitted November 21, 1961

Heteroorganic compounds, for example $R_2\mathfrak{E}(OOCR)_2$, react with a diazoalkane in the following way:



$$+2RCOOCH_3+2N_2$$

Hydrolysis by the usual procedures, for example of $R_2Sn(OOCR)_2$ gives, as is well known, a complex mixture of organotin products [1]. In our case, growth of the heteroelement–oxygen chain takes place, with the isolation of individual products in stages and with the preservation of the terminal RCOO group, for example in the case of $(n\text{-}C_4H_9)_2Sn(OOCCH_3)_2$.

The monomer [b.p. 142-145° (100 mm)] → dimer (m.p. 58-60°) → tetramer (m.p. 138-139°) → octamer (decomp. p. above 200°), and so on.

The reaction will be illustrated here using two elements (Sn, Pb) as examples, but, so we are convinced, it may be extended to other heteroorganic compounds containing at least two saponifiable groups on the heteroelement (for example, $R_2Si(OOCR)_2$ or $RTl(OOCR)_2$, and so on.

With diazomethane. (a) $2R_2SnX_2$ (I) – $X(R)_2Sn-O-Sn(R)_2X$ (II). For (II) found: C 39.68; 39.74; H 6.89; 6.99; Sn 39.91; 40.05%; mol.wt. 591. $C_{20}H_{42}O_5Sn_2$. Calculated: C 40.04; H 7.007; Sn 39.60%; mol.wt. 599.4.

(b) $2X(R)_2Sn-O-Sn(R)_2X$ (II) → $X(R)_2Sn-[O(R)_2Sn]_3-X$ (III). For (III) found: C 39.26; 39.40; H 7.14; 7.24; Sn 42.78%; mol.wt. 1109. $C_{36}H_{78}O_7Sn_4$. Calculated: C 39.37; H 7.11; Sn 43.27%; mol.wt. 1096.8.

(c) $2X(R)_2Sn-[O(R)_2Sn]_3-X$ (III) → $X(R)_2Sn-[O(R)_2Sn]_7-X$ (IV). For (IV): Found, C 39.03; 39.08; H 7.19; 7.22; Sn 45.8; 45.51%; mol.wt. 2156. $C_{68}H_{150}O_{11}Sn_8$. Calculated: C 39.02; H 7.17; Sn 45.41%; mol.wt. 2091.6. (Everywhere $R = n\text{-}C_4H_9$; $X = OOCCH_3$).

(d) $2R_2PbX_2$ (I) → $X(R)_2Pb-O-Pb(R)_2X$ (II). [$R = C_6H_5$; $X = OOCCH(CH_3)_2$]. For (II), decomp. p 240°. Found: C 42.39; 42.27; H 3.80; 3.77; Pb 45.39; 45.37%. $C_{32}H_{34}O_5Pb_2$. Calculated: C 42.09; H 3.73; Pb 45.41%.

With diazoethane and diazobutane, the same product (II) was obtained; decomp. p 240°. Found: Pb 45.46; 45.34; 45.40%.

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1. S. M. Zhivykhin, É. D. Dudikova and V. V. Kireev, Zh. obshch. khimii, 31, 3106 (1961).

GENERAL MEETING OF THE DIVISION OF CHEMICAL SCIENCES OF THE ACADEMY OF SCIENCES OF THE USSR, SEPTEMBER 21, 1961

Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk,
No. 12, pp. 2256-2257, December, 1961

On September 21, 1961, the General Meeting of the Division of Chemical Sciences of the Academy of Sciences of the USSR was held. Academician V. A. Kargin presented a lecture on the subject "Synthetic Materials Based on Polymers". Pointing out that the main tasks in the polymer field are the creation of industrial materials and the solution of problems connected with biologically active polymers, the lecturer emphasized that the direction of general scientific investigations was determined by these same tasks. Even with the existence and rapid growth of the production of polymeric substances, particular importance was possessed not only by the search for new polymers but also by methods of modifying and improving existing polymeric substances. The fight against the degradation of polymeric materials was as fundamental as the fight against the corrosion of metals, and the successful solution of this problem—the stabilization of polymers—depended in the first place on the elucidation of the mechanism of degradation of polymers under the influence of various agents (chemicals, heat, light, radiation, etc.). Since the degradation processes were generally initiated by impurities, the purity of the polymers and, consequently, the search for the most effective methods of purifying the monomers, had a particular importance. Finally, copolymerization or grafting enabled substances with new properties to be obtained by the union of different monomers. This is a problem of modifying the polymers.

Problems of treatment arising in the conversion of the polymers to working materials and finished articles had changed very much in recent years and were being transformed from methods of imparting shape into methods of imparting structure. The discovery of diverse and highly-organized structures in polymers indicated the possibility of varying the properties of polymers widely by physical methods. Hence, success in the field of treatment of polymers is connected with the development both of the theory of rheology and the theory of the origin of structure. An absolutely special and important place was occupied by reinforced materials, since only they made it possible to combine the resilient properties of polymers with the strength properties of ordinary solid bodies. Finally, the lecturer mentioned, the wide use of polymers demands the creation of a "sopromata" and metrology for this class of materials.

In addition to the large-tonnage polymers, there is a large and rapidly growing group of polymers for very diverse purposes, frequently expensive and manufactured in small amounts, but, as a rule, irreplaceable. These include, said V. A. Kargin, heat-stable materials, particularly rubbers, ion-exchange and complexone resins, primarily for the selective isolation and separation of metals and a number of organic substances, physiologically active polymers, light-sensitive polymers, semi-conductor polymers, polymers with an extremely high chemical stability, and so on. The widening of the circle of these substances requires, in the first place, the creation of new polymers and, connected with this, wide research in the fields both of synthesis and polymerization. The search for polymers stable to high temperatures, generally carried out in the field of fluorine-containing substances, organosilicon polymers, and their analogs, and polymers containing cyclic and linear groups with conjugated double bonds, is of great importance. Unfortunately, the lecturer said, it is in this field that the absence of wide investigations and new ideas is most powerfully felt. In the creation of new polymers, polymerization still plays a greater role than direct synthesis and continues to remain the leading field of polymer chemistry. The use of complex catalytic systems and new methods of polymerization—in the first place, polymerization in the solid state, made it possible to achieve further success both in obtaining regularly constructed chains of complex structure, in particular optically active polymers and regularly constructed co-polymers, and in the polymerization of a number of cyclic compounds. Widening the circle of polyolefins and rubbers was also connected with successes in polymerization.

In the lecturer's opinion, the problem of creating inorganic materials possessing a complex of mechanical properties close to those of polymers, was completely separate. On this question, only the problems were still being formulated, and no clear methods for their solution existed as yet.

Academician M. M. Shemyakin presented a paper on "The Chemistry of Natural Biologically Important Compounds". The main task in this connection, he said, is the study of the physicochemical nature of living processes and phenomena and, above all, the investigation of those substances the transformations of which constitute the material basis of these processes and determine their course. A development of these problems would lead from new directions to the solution of important scientific and practical questions of health (the fight against infections, tumor and nerve diseases, radiation sicknesses, affections of the cardiac vascular system, and other causes of premature old age), agriculture (the regulation and stimulation of the growth of animals and plants, and also the creation of new valuable forms with given properties in order to increase agricultural production and to fundamentally change its nature in the direction of mechanization and increased productivity), various branches of industry, in particular, the preserving and food industries (in order to fundamentally change the technology, for example, of the prolonged storage of food products without using refrigeration). The chemistry of natural biologically active compounds must be developed in the directions of isolation, the study of structure, synthesis, and elucidation of the connection between structure and biological activity, and also the essence of the mechanism of the action of proteins, carbohydrates, lipids (particularly their complex compounds), nucleic acids, alkaloids, vitamins, antibiotics, hormones, terpenoids, nd other types of natural substances having decisive importance in determining the normal vital activity of man, animals, and plants. Not less important is the development of investigations on the synthesis and study of synthetic medicinal substances and regulators of the reproduction growth, development, and regulation of the functions of animals, plants and microorganisms. All the compounds valuable in practice, in the first place antibiotics, hormones, vitamins and synthetic medical substances, must rapidly undergo many-sided trials with the simultaneous development of economically favorable technological methods for their preparation for the subsequent organization of industrial production. An important direction for the investigation, said the lecturer, must be the chemical, biochemical, and microbiological study of fermentative processes in order to develop the fermentation industry for producing chemical products of practical importance. A successful development of investigations in the field of bioorganic and biophysical chemistry is impossible without the development of new methods and procedures of working and without the continual perfection of existing methods. This was indissolubly connected with new original apparatus. Other necessary conditions for successful development in this field, M. M. Shemyakin emphasized, were the creation of qualified personnel possessing a knowledge of bases and methods not only in the field of chemistry but also in the field of disciplines intertwined with it, above all, physics and biology.

In the discussions on the papers, many members took part. Corresponding Member I. P. Alimarin mentioned the importance of the problem of the purity of materials and the development of methods for testing substances of a high degree of purity. Corresponding Member M. M. Koton pointed to the importance of the development of theoretical questions connected with the creation of new model polymers with a high degree of purity and a strictly determined structure. Academician V. I. Spitsyn expressed his opinion on the necessity for paying great attention to investigations of radiation effects on the polymerization process and polymeric products. Corresponding Member B. V. Deryagin emphasized the importance of scientific contacts with physicists, such as were successfully carried out in working on polymer problems in the Institute of High Molecular Weight Compounds. Academician I. L. Knunyants and Corresponding Member V. V. Korshak mentioned the necessity for putting the question of the creation of special laboratories for the development of monomers. Academician M. I. Kabachnik developed a series of considerations on the organization of the production of some new laboratory apparatuses. A number of observations on the lectures were made by Corresponding Member G. B. Bokii, Doctor of Chemical Sciences A. A. Akhrem, Academician A. N. Frumkin, Corresponding Member N. K. Kochetkov, and others.

MISSING PAGES ARE INDEX PAGES
WHICH HAVE BEEN PHOTOGRAPHED
AT THE BEGINNING OF THE VOLUME(S)

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.- Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.-Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

NOTE: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. —Publisher.

Soviet Journals Available in Cover-to-Cover Translation

ABBREVIATION	RUSSIAN TITLE	TITLE OF TRANSLATION	PUBLISHER	TRANSLATION BEGAN Vol.	Issue	Year
AÉ	Atomnaya énergiya	Soviet Journal of Atomic Energy	Consultants Bureau	1	1	1956
Akust. zh.	Akusticheskii zhurnal	Soviet Physics – Acoustics	American Institute of Physics	1	1	1955
	Antibiotiki	Antibiotics	Consultants Bureau	4	1	1959
Astr(on). zh(urn).	Astronomicheskii zhurnal	Soviet Astronomy–AJ	American Institute of Physics	34	1	1957
Avto(mat). svarka	Avtomaticheskaya svarka	Automatic Welding	British Welding Research Association (London)		1	1959
	Avtomatika i Telemekhanika	Automation and Remote Control	Instrument Society of America	27	1	1956
	Biofizika	Biophysics	National Institutes of Health*		1	1957
	Biokhimiya	Biochemistry	Consultants Bureau	21	1	1956
Byull. éksp(erim). biol. i med.	Byulleten' éksperimental'noi biologii i meditsiny	Bulletin of Experimental Biology and Medicine	Consultants Bureau	41	1	1959
DAN (SSSR) / Dokl(ady) AN SSSR	Doklady Akademii Nauk SSSR	The translation of this journal is published in sections, as follows:				
		Doklady Biochemistry Section	American Institute of Biological Sciences	106	1	1956
		Doklady Biological Sciences Sections (Includes: Anatomy, biophysics, cytology, ecology, embryology, endocrinology, evolutionary morphology, genetics, histology, hydrobiology microbiology, morphology, parasitology, physiology, zoology sections)	American Institute of Biological Sciences	112	1	1957
		Doklady Botanical Sciences Sections (Includes: Botany, phytopathology, plant anatomy, plant ecology, plant embryology, plant physiology, plant morphology sections)	American Institute of Biological Sciences	112	1	1957
		Proceedings of the Academy of Sciences of the USSR, Section: Chemical Technology	Consultants Bureau	106	1	1956
		Proceedings of the Academy of Sciences of the USSR, Section: Chemistry	Consultants Bureau	106	1	1956
		Proceedings of the Academy of Sciences of the USSR, Section: Physical Chemistry	Consultants Bureau	112	1	1957
		Doklady Earth Sciences Sections (Includes: Geochemistry, geology, geophysics, hydrogeology, mineralogy, paleontology, petrography, permafrost sections)	American Geological Institute	124	1	1959
		Proceedings of the Academy of Sciences of the USSR, Section: Geochemistry	Consultants Bureau	106-123	1-6	1957-1958
		Proceedings of the Academy of Sciences of the USSR, Sections: Geology	Consultants Bureau	106-123	1-6	1957-1958
		Doklady Soviet Mathematics	The American Mathematics Society	131	1	1961
		Soviet Physics–Doklady (Includes: Aerodynamics, astronomy, crystallography, cybernetics and control theory, electrical engineering, energetics, fluid mechanics, heat engineering, hydraulics, mathematical physics, mechanics, physics, technical physics, theory of elasticity sections)	American Institute of Physics	106	1	1956
		Proceedings of the Academy of Sciences of the USSR, Applied Physics Sections (does not include mathematical physics or physics sections)	Consultants Bureau	106-117	1	1956-1957
Derevoobrabat. prom-st'.	Derevoobrabatyvayushchaya promyshlennost'	Wood Processing Industry	Timber Development Association (London)		9	1959
	Élecktrosvyaz	Telecommunications	Massachusetts Institute of Technology*		1	1957
Éntom(ol). oboz(renie)	Éntomologicheskoe obozrenie	Entomological Review	American Institute of Biological Sciences	38	1	1959
Farmakol. (i) toksikol(ogiya)	Farmakologiya i toksikologiya	Pharmacology and Toxicology	Consultants Bureau	20	1	1957
FMM	Fizika metallov i metallovedenie	Physics of Metals and Metallography	Acta Metallurgica*	5	1	1957
Fiziol. zhurn. SSSR (im. Sechenova)	Fiziologicheskii zhurnal im. I. M. Sechenova	Sechenov Physiological Journal USSR	National Institutes of Health*		1	1957
Fiziol(ogiya) rast.	Fiziologiya rastenii	Plant Physiology	American Institute of Biological Sciences	4	1	1957
	Geokhimiya	Geochemistry	The Geochemical Society		1	1958
FTT	Fizika tverdogo tela	Soviet Physics–Solid State	American Institute of Physics	1	1	1959
Izmerit. tekh(nika)	Izmeritel'naya tekhnika	Measurement Techniques	Instrument Society of America		1	1959
Izv. AN SSSR. O(td). Kh(im). N(auk)	Izvestiya Akademii Nauk SSSR: Otdelenie khimicheskikh nauk	Bulletin of the Academy of Sciences of the USSR: Division of Chemical Sciences	Consultants Bureau		1	1952

Life Sciences

Chemical Sciences

Earth Sciences

Mathematics

Physics

continued

Izv. AN SSSR, O(td). T(ekhn). N(auk): Met(all). i top.	(see Met. i top.)				
Izv. AN SSSR Ser. fiz(ich).	Izvestiya Akademii Nauk SSSR: Seriya fizicheskaya	Bulletin of the Academy of Sciences of the USSR: Physical Series	Columbia Technical Translations	1	1954
Izv. AN SSSR Ser. geofiz.	Izvestiya Akademii Nauk SSSR: Seriya geofizicheskaya	Bulletin (Izvestiya) of the Academy of Sciences USSR: Geophysics Series	American Geophysical Union	1	1954
Izv. AN SSSR Ser. geol.	Izvestiya Akademii Nauk SSSR: Seriya geologicheskaya	Izvestiya of the Academy of Sciences of the USSR: Geologic Series	American Geological Institute	1	1958
Kauch. i rez.	Kauchuk i rezina	Soviet Rubber Technology	Research Association of British Rubber Manufacturers 18	1	1959
	Kinetika i kataliz	Kinetics and Catalysis	Consultants Bureau 1	3	1960
	Koks i khimiya	Coke and Chemistry USSR	Coal Tar Research Association (Leeds, England)	1	1958
Kolloidn. zh(urn).	Kolloidnyi zhurnal	Colloid Journal	Consultants Bureau 14	1	1952
	Kristallografiya	Soviet Physics -- Crystallography	American Institute of Physics 2	1	1957
Metalov. i term. obrabot. metal.	Metallovedenie i termicheskaya obrabotka metallov	Metal Science and Heat Treatment of Metals	Acta Metallurgica 6	1	1958
	Metallurg	Metallurgist	Acta Metallurgica	1	1957
Met. i top.	Metallurgiya i topliva	Russian Metallurgy and Fuels	Eagle Technical Publications	1	1960
Mikrobiol.	Mikrobiologiya	Microbiology	American Institute of Biological Sciences 26	1	1957
OS	Optika i spektroskopiya	Optics and Spectroscopy	American Institute of Physics	6	1959
	Pochvovedenie	Soviet Soil Science	American Institute of Biological Sciences	1	1958
	Priborostroenie	Instrument Construction	British Scientific Instrument Research Association	1	1959
Pribory i tekhn. éks(perimenta)	Pribory i tekhnika éksperimenta	Instruments and Experimental Techniques	Instrument Society of America	1	1957
Prikl. matem. i mekh.	Prikladnaya matematika i mekhanika	Applied Mathematics and Mechanics	American Society of Mechanical Engineers	1	1958
PTÉ	(see Pribory i tekhn. éks.)				
	Problemy Severa	Problems of the North	National Research Council of Canada		
Radiotekh.	Radiotekhnika	Radio Engineering	Massachusetts Institute of Technology* 12	1	1957
Radiotekh. i élektronika	Radiotekhnika i élektronika	Radio Engineering and Electronics	Massachusetts Institute of Technology* 2	1	1957
	Stanki i instrument	Machines and Tooling	Production Engineering Research Assoc.	1	1959
	Stal'	Stal (In English)	Iron and Steel Institute	1	1959
Stek. i keram.	Steklo i keramika	Glass and Ceramics	Consultants Bureau 13	1	1956
Svaroch. proiz-vo	Svarochnoe proizvodstvo	Welding Production	British Welding Research Association	4	1959
Teor. veroyat. i prim.	Teoriya veroyatnostei i ee primenenie	Theory of Probability and Its Applications	Society for Industrial and Applied Mathematics	1	1956
Tsvet. Metally	Tsvetnye metally	Nonferrous Metals	Primary Sources	1	1960
UFN	Uspekhi fizicheskikh Nauk	Soviet Physics -- Uspekhi (partial translation)	American Institute of Physics 66	1	1958
UKh	Uspekhi khimii	Russian Chemical Reviews	The Chemical Society (London)	1	1960
UMN	Uspekhi matematicheskikh nauk	Russian Mathematical Surveys	London Mathematical Society 15	1	1960
Usp. fiz. nauk	(see UFN)				
Usp. khim(ii)	(see UKh)				
Usp. matem. nauk	(see UMN)				
Usp. sovr. biol.	Uspekhi sovremennoi biologii	Russian Review of Biology	Oliver and Boyd	48	1959
Vest. mashinostroeniya	Vestnik mashinostroeniya	Russian Engineering Journal	Production Engineering Research Assoc.	4	1959
Vop. gem. i per. krovi	Voprosy gematologii i perelivaniya krovi	Problems of Hematology and Blood Transfusion	National Institutes of Health*	1	1957
Vop. onk.	Voprosy onkologii	Problems of Oncology	National Institutes of Health*	1	1957
Vop. virusol.	Voprosy virusologii	Problems of Virology	National Institutes of Health*	1	1957
Zav(odsk). lab(oratoriya)	Zavodskaya laboratoriya	Industrial Laboratory	Instrument Society of America 25	1	1959
ZhAKh Zh. anal(it). khimii	Zhurnal analiticheskoi khimii	Journal of Analytical Chemistry USSR	Consultants Bureau 7	1	1952
ZhETF Zh. éksperim. i teor. fiz.	Zhurnal éksperimental'noi i theoreticheskoi fiziki	Soviet Physics--JETP	American Institute of Physics 28	1	1955
ZhFKh Zh. fiz. khimii	Zhurnal fizicheskoi khimii	Russian Journal of Physical Chemistry	The Chemical Society (London)	7	1959
ZhMÉI Zh(urn). mikrobiol. épidemiol. i immunobiol.	Zhurnal mikrobiologii, épidemiologii i immunobiologii	Journal of Microbiology, Epidemiology and Immunobiology	National Institutes of Health*	1	1957
ZhNKh Zh(urn). neorgan(ich). khim(ii)	Zhurnal neorganicheskoi khimii	The Russian Journal of Inorganic Chemistry	The Chemical Society (London)	1	1959
ZhOKh Zh(urn). obshch(ei) khimii	Zhurnal obshchei khimii	Journal of General Chemistry USSR	Consultants Bureau 19	1	1949
ZhPKh Zh(urn). prikl. khimii	Zhurnal prikladnoi khimli	Journal of Applied Chemistry USSR	Consultants Bureau 23	1	1950
ZhSKh Zh(urn). strukt. khimii	Zhurnal strukturnoi khimii	Journal of Structural Chemistry	Consultants Bureau 1	1	1960
ZhTF Zh(urn). tekhn. fiz.	Zhurnal teknicheskoi fiziki	Soviet Physics--Technical Physics	American Institute of Physics 26	1	1956
Zh(urn). vyssh. nervn. deyat. (im. Pavlova)	Zhurnal vysshei nervnoi deyatel'nosti (im. I. P. Pavlova)	Pavlov Journal of Higher Nervous Activity	National Institutes of Health*	1	1958

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